



**Ernest Orlando Lawrence**  
**Berkeley National Laboratory**  
1 Cyclotron Road, 70R0108B, Berkeley CA 94720-8168  
(510) 486-4636; fax: (510) 486-4260

April 28, 2005

Mr. Tien Q. Duong  
5G-030, EE-32  
Forrestal Building  
U.S. Department of Energy  
Washington D.C. 20585

Dear Tien:

Here is the second-quarter FY 2005 report for the Batteries for Advanced Transportation Technologies (BATT) Program. This report and prior Program reports can be downloaded from <http://berc.lbl.gov/BATT/BATTreports.html>.

Sincerely,

Frank McLarnon  
Manager  
BATT Program

cc:	J. Barnes	DOE/OFCVT
	D. Howell	DOE/OFCVT
	E. Wall	DOE/OFCVT
	K. Abbott	DOE-BSO

LBID-2563 (2)

# **BATT TASK 1 CELL DEVELOPMENT**

## **TASK STATUS REPORT**

**PI, INSTITUTION:** V. Battaglia, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Cell Development - Cell Fabrication and Testing

**SYSTEMS:** Graphite/LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> (high-energy, high-voltage Li-ion), Graphite/LiFePO<sub>4</sub> (low-cost Li-ion), and Graphite/LiMn<sub>2</sub>O<sub>4</sub> (high-power Li-ion)

**BARRIERS:** Li-ion systems meeting performance, abuse, and life targets.

**OBJECTIVES:** The primary objective is to establish a test vehicle for the evaluation of new materials for high-power or high-energy, low-cost Li-ion cells.

**APPROACH:** The testing of novel materials in a standard cell with preset protocols will provide the necessary link between the invention of novel battery components and the diagnostic evaluation of failure modes, and will accelerate the development of EVs, HEVs and FCEVs. Novel components will be developed in BATT Program Tasks 2, 3, and 4 (anodes, electrolytes, and cathodes) for baseline cell chemistries. These components are incorporated into a standardized cell, and then tested using a consistent protocol to determine cell capacity, energy, power, and lifetime characteristics. Tested cell components are then delivered to appropriate investigators involved with BATT Program diagnostic projects.

**STATUS OCT. 1, 2004:** Further benchmarking of the low-cost Li-ion baseline cell including high-temperature aging will be carried out with larger cell sets to demonstrate reproducibility. Diagnostic analysis of cell components from this study will be combined with those from previous cells to lend insight into the degradation mechanism occurring on the natural graphite electrode in the presence of LiFePO<sub>4</sub>.

**EXPECTED STATUS SEPT. 30, 2005:** Performance measurements on the candidate sources of LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> will be carried out and compared to the baseline material from Seimi. Room-temperature benchmarking of this baseline chemistry will be completed. In addition, half-cell studies of LiMn<sub>2</sub>O<sub>4</sub> in LiBOB-containing electrolyte for the high-power baseline cell will be carried out. Pouch cells from HQ will be benchmarked with regard to performance and aging and distributed to the diagnostic projects for analysis. Electrodes and cells will be prepared and tested in support of modeling and synthesis projects for the various baseline systems.

**RELEVANT USABC GOALS:** Specific power 780 W/L, 15 year life, < 23% power fade.

### **MILESTONE:**

- |   |      |
|---|------|
| (a) Test 6 LiFePO <sub>4</sub> pouch cells from HQ  | 3/05 |
| (b) Benchmark LiMn <sub>2</sub> O <sub>4</sub> in LiBOB and LiPF <sub>6</sub> based electrolyte | 6/05 |

## PROGRESS TOWARD MILESTONES

### Progress toward milestones

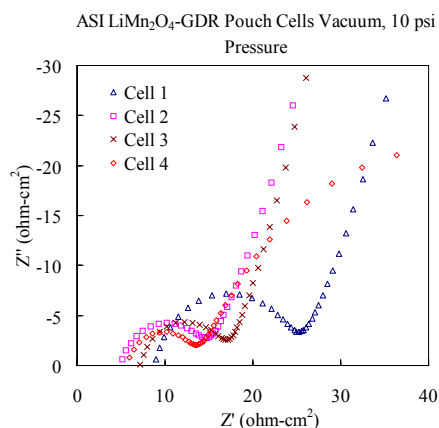
*Modifications to Milestones* - Since the FY 2005 AOP was written, there have been some modifications to the expected progress and milestones as reported in the previous quarter.

### Progress toward altered milestones

(a) **Completed.** Karim Zaghib of Hydro Quebec sent two batches of pouch cells to LBNL for independent testing. One batch arrived in November 2004 and the other batch in February 2005. At the time of their arrival, we were still reorganizing our laboratory. The reorganization was mostly completed by the end of January. Thus, testing the HQ cells began end-of-January/early-February. As we found, HQ has had some problems sealing pouch cells; also, as a request from the previous PI, pouch cells were sent without formation. The problem with that is the possible corrosion of the copper current collector as the samples sit in storage awaiting testing. Upon testing the HQ cells we found that they would either have no charge capacity or would charge indefinitely. Of 22 pouch cells, we found only one that could complete the new BATT Electrode Characterization Test Protocol and that cell had a very high resistance ( $300 \text{ ohm-cm}^2$ ). These problems with the cells were conveyed to K. Zaghib, and we agreed that he would stop sending pouch cells until they could successfully seal them and that they would send laminates from a new, large coater that recently came on-line. Our efforts to make pouch cells from laminates will be intensified during the next quarter.

(b) **On-going.** An important task for this group is the ability to make representative cells. Representative means that the cells give good rate performance and age with a minimum effect from contamination. The previous quarter focused on setting up the laboratory, this quarter focused on building cells from the ground up. To go along with the milestone, we have selected the spinel baseline as a target system to demonstrate our ability to reproducibly make full cells. Along that path we made coatings of several chemistries including  $\text{LiFePO}_4$ ,  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ,  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$ ,  $\text{LiMn}_2\text{O}_4$ , and GDR-AB11.  $\text{LiFePO}_4$  could be tested against laminates produced by HQ;  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  could be tested against laminates made in the ATD Program;  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  could be tested against laminates made in this group just prior to the reorganization; and  $\text{LiMn}_2\text{O}_4$  was coated because it is the target chemistry. This analysis also allowed us to determine coating quality as a function of active material. Previous results indicated that some of the coatings, especially the  $\text{LiFePO}_4$ , require an initial carbon coating on the current collector to achieve good performance. We are now finding that this can be circumvented with proper mixing and calendaring.

Here we describe our latest capabilities for making reproducible spinel pouch cells. Reproducible capacity is not good enough for our mission: we need to demonstrate reproducible power. One test of this is criterion electrochemical impedance spectroscopy (EIS). Four cells were assembled and formed and then evaluated with EIS on a Solartron. The figure demonstrates our present capabilities. One sees that graphs of cells 2 and 3 fall nearly on top of each other with essentially equivalent ohmic drop and interfacial impedance. Cell 4 appears to have a different low-frequency impedance and cell 1 suffers from high ohmic and interfacial impedance. Although all four cells did not perform identically, we take comfort in the fact that the two cells that perform the same, perform the best. We will continue to work on this task into the next quarter.



## TASK STATUS REPORT

**PI, INSTITUTION:** T.J. Richardson, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Cell Development - Materials Characterization, Overcharge Protection, Cathode Development

**SYSTEMS:** High-voltage, high-power: Gr/LiBOB+ $\gamma$ BL:EA/LiMn<sub>2</sub>O<sub>4</sub>  
Low-voltage, high-stability: Gr/LiPF<sub>6</sub>+EC:DEC/LiFePO<sub>4</sub>

**BARRIER:** Short lifetimes, poor abuse tolerance

**OBJECTIVES:** Support cell development and diagnostics tasks through structural characterization of active electrode components before, during, and after cycling. Protect cells against degradation and failure due to overcharging by means of lightweight, inexpensive protection mechanisms. Investigate particle isolation and oxygen loss mechanisms in composite electrodes. Synthesize and evaluate alternative electrode materials.

**APPROACH:** Address primary causes of power and capacity fading by correlating them with changes in the composition and structure of active materials and composite electrodes. Techniques employed include x-ray diffraction (XRD), vibrational spectroscopy, and electroanalytical testing. Continue to develop a reversible overcharge protection mechanism based on components that automatically short overcharged cells. Discover improved cell systems through a limited program of synthesis and evaluation.

**STATUS OCT. 1, 2004:** Composition and structural analyses of BATT Task 1.1 electrodes have contributed to our understanding of failure and degradation modes in the baseline systems. Electroactive conducting polymers capable of providing overcharge protection in Li-ion cells with cathode potentials above 4.0 V have been characterized. New cathode materials were synthesized and evaluated for introduction into BATT chemistries.

**EXPECTED STATUS SEPT. 30, 2005:** Improvements in chemistry, morphology and distribution of highly conducting polymers will permit protection of high-power cells against overcharging at rates as high as 3C. High-rate electrode materials will have been characterized for stability and compatibility with electrolytes.

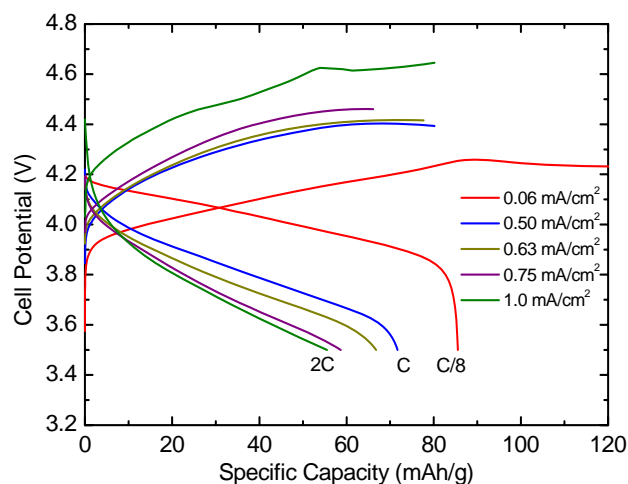
**RELEVANT USABC GOALS:** Abuse tolerance to cell overcharge and short circuit, 30 ohm-cm<sup>2</sup> area-specific impedance.

**MILESTONE:**

Protect LiMn<sub>2</sub>O<sub>4</sub> cells against 10 cycles of 5% overcharge at 3C or higher. (July 2005)

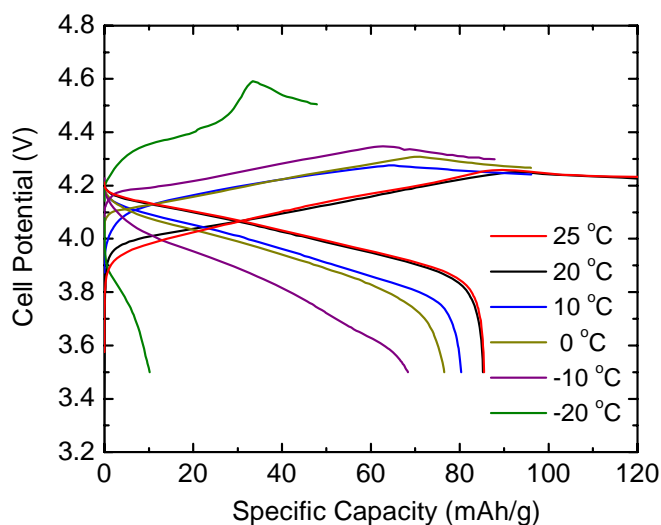
## PROGRESS TOWARD MILESTONE

The performance of a bilayer conducting polymer composite separator impregnated with poly(9,9-dioctylfluorene) on the cathode side and poly(3-butylthiophene) on the anode side in a Li cell with a spinel-type  $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$  cathode was studied at different charge-discharge rates. Because the resistance across the polymer-impregnated separator varies with current density, the potential at which a cell is shorted increases with the charging rate (Fig. 1).



**Figure 1.** Variable-rate charge-discharge curves for protected  $\text{Li}/\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$  cell.

A low-temperature study of the same cell illustrates the ability of the polymer composite to protect the cell down to at least  $-20^\circ\text{C}$  (Fig. 2). The electrolyte resistance becomes significant at  $10^\circ\text{C}$ , causing the short to appear early, then the short gradually grows less resistant as the polymer is oxidized. Some protection is afforded even at  $-20^\circ\text{C}$ , where the electrolyte (LP40) is beginning to solidify.



**Figure 2.** Variable-temperature charge-discharge curves for protected  $\text{Li}/\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$  cell.

## TASK STATUS REPORT

**PI, INSTITUTION:** K. Zaghib, Hydro-Québec (IREQ)

**TASK TITLE - PROJECT:** Cell Development - Lithium-Ion Polymer Batteries with Low-Cost Materials

**SYSTEMS:** Low-cost Li-ion

**BARRIER:** High cost of Li-ion batteries

**OBJECTIVES:** Fabricate Li-ion/polymer cells ( $4\text{ cm}^2$  area) using cell chemistries proposed by DOE, and send 50% of the total cells to LBNL for testing. Optimize gel formation as a function of the % plasticizer content, optimize the thermal cross-linked temperature by using new polymer with ionic liquid or liquid electrolyte as plasticizer. Determine the conductivity of gel electrolyte as a function of plasticizer content, particularly at low temperature. Study the interface of gel electrolyte in contact with the electrode active materials.

**APPROACH:** Our approach is to synthesize and coat electrodes (both anode and cathode) with low-cost materials, and to evaluate these materials in Li-ion/polymer cells. Additional work will focus on gel polymers, as well as studies to identify an appropriate salt and solvent to increase the performance and charge/discharge rate of Li cells at low temperatures. The gel electrolyte will be compared to a liquid electrolyte (100%) by measurements in half cells and Li-ion polymer cells at low temperatures.

**STATUS OCT. 1, 2004:** We will optimize the composition of anode (natural graphite, fibers) and cathode materials in the electrodes as a function of the water-soluble binder (WSB) (no fluoride), with the goal of reducing the amount of binder by 50% compared to standard electrodes with PVDF. To reduce the amount of binder and the cost of the coating, we will demonstrate a new coating process using WSB in the anode and cathode ( $\text{LiFePO}_4$ ). Also, we expect to show the effect the soluble WSB on other baselines chemistries ( $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ ). A study of the effects of PVDF and WSB in electrodes to improve the safety aspect of the battery will be completed. We expect to provide primary cycling data (including PNGV protocol) from Li-ion/polymer cells containing WSB and a low-cost Li salt. We will continue to develop carbon-coated  $\text{LiFePO}_4$  (Phostech) with higher tap density.

**EXPECTED STATUS SEPT. 30, 2005:** We will determine the composition of gel electrolytes, which are based on a new high-viscosity polyether gel, as a function of the amount of ionic liquid (molten salt) or liquid electrolyte used as plasticizers. These plasticizers should be beneficial in reducing the amount of polymer and to increase the safety of the cell, and will be compared to results obtained with electrodes containing PVDF and WSB. We will optimize the gel electrolyte with different anodes based on hard carbon, soft carbon, and graphite to select a good candidate for low-temperature and high-rate applications. The amounts of cathode material and gel electrolyte will be optimized to increase the high-rate performance of  $\text{LiFePO}_4$ , and other baselines chemistries ( $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ ). ARC safety tests using a new gel electrolyte in contact with anodes and cathodes will be evaluated in collaboration with J. Dahn, and details are under discussion. We expect to provide cycling data, including the PNGV protocol, in Li-ion polymer cells that contain gel electrolyte based on polymer-ionic liquid, polymer-liquid electrolyte, and 100% liquid electrolyte.

**RELEVANT USABC GOALS:** Specific power 300 W/kg, 10-year life, < 20% capacity fade.

**MILESTONES:** 1) Identify an ionic liquid with low-cost, high-viscosity polymer (April 2005). 2) Deliver thirty (30) cells to LBNL (10 cell every four months). 3) Produce  $\text{LiFePO}_4$  with high tap density at Phostech. (February 2005).

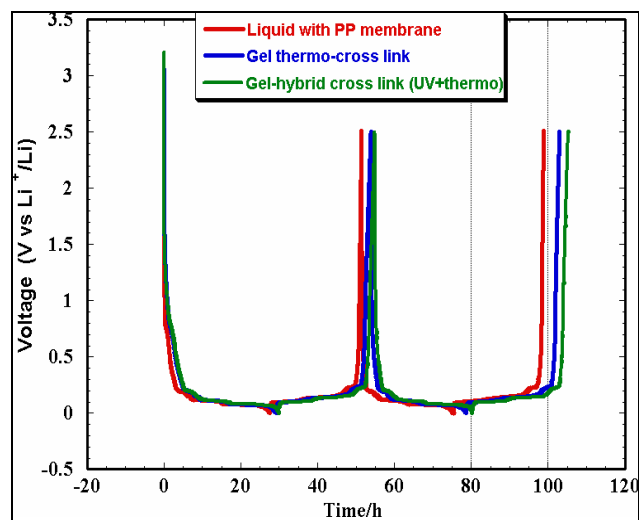
## PROGRESS TOWARD MILESTONE

During this quarter we focused on the effect of the thickness of the iron phosphate cathode on electrochemical performance. The coated cathode films are based on iron phosphate material with standard PVDF binder. This batch of coated cathodes will be used to study the effect of temperature on cycle life. The temperature range is between 60-40°C.

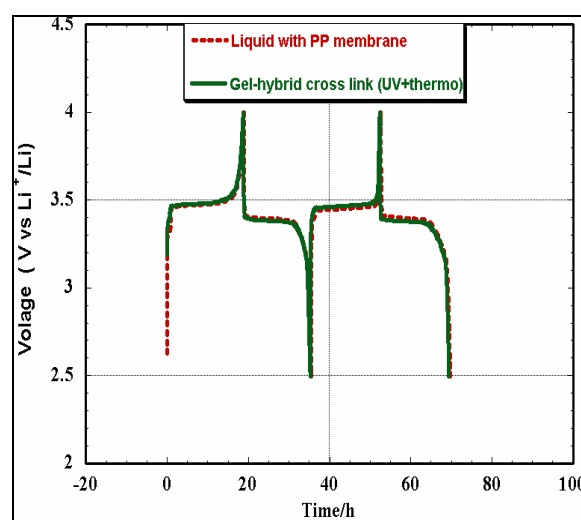
The second goal is to validate a new polymer gel having low molecular weight in cells with graphite anode and  $\text{LiFePO}_4$  cathode. The polymer is coated on a polypropylene (PP) separator and cross-linked by two different methods: a) thermally at 60°C for 1 h, b) hybrid cross-link by thermal and UV. For the second method, the polymer electrolyte was cross-linked first with UV, sealed in the cell, and then cross-linked thermally at 60°C/h. In both cases, the polymer electrolyte was first filled in the pores of the electrodes before UV cross-linking. The gel polymer prepared by using these methods is expected to improve the interface between the electrodes and the polymer electrolyte.

Half cells of  $\text{Li/EC-DMC-LiPF}_6$  gel/graphite (anode cell) and  $\text{Li/EC-DMC-LiPF}_6$  gel/ $\text{LiFePO}_4$  (cathode cell) that contain thermally crosslinked and hybrid crosslinked gels were compared with standard liquid cells.

Efforts will continue to fabricate 30 Li-ion gel-electrolyte cells containing  $\text{LiFePO}_4$  and other BATT baselines chemistries ( $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ ) for evaluation by LBNL. Similar cells will also be evaluated at Hydro-Québec.



**Figure 1.** Cycles 1-2 of anode half-cells with thermal gel polymer, with hybrid gel polymer and with liquid standard in EC-DEC- $\text{LiPF}_6$ .



**Figure 2.** Cycles 1-2 of cathode  $\text{LiFePO}_4$  half cells with hybrid gel polymer electrolyte compared to liquid standard in EC-DEC- $\text{LiPF}_6$ .

Figure 1 shows the first 2 cycles at C/24 of the anode cells at 25°C. For the anode cell with gel obtained thermally, the initial (first-cycle) coulombic efficiency is 85% and the reversible capacity is 342 mAh/g. For the anode cell with hybrid crosslink gel, the coulombic efficiency is 83% with a reversible capacity of 347 mAh/g. The standard anode cell shows 86% and 337 mAh/g, respectively, coulombic efficiency and reversible capacity.

For the cathode  $\text{LiFePO}_4$  half cells, a comparable result (Fig. 2) was obtained for a hybrid-polymer gel cell and a Celgard liquid cell, *i.e.*, 88% coulombic efficiency for both cells and 156 mAh/g and 155 mAh/g, respectively, for the reversible capacity. These data confirm the good performance of the gel polymer obtained by the hybrid method.

For our last goal,  $\text{LiFePO}_4$  cathode films with PVDF binder of different thicknesses were sent to LBNL for evaluation. Ten (10) flat cells and ten (10) coin-type cells with new sealing polymer will be sent by the end of April; these cells will be formed at IREQ. We are working to resolve the problem of long-term sealing of the flat cells. The dry room at the Hydro-Québec-Shawinigan facility was repaired and opened for coating in April 2005 after four months down time. HQ financed 100% of the repair work of this dry room.

## TASK STATUS REPORT

**PI, INSTITUTION:** D. Wheeler and J. Harb, Brigham Young University

**TASK TITLE – PROJECT:** Design, Optimization, and Fabrication of Li-ion Electrodes for High Power Applications

**SYSTEM:** Low-voltage, high-stability: Gr/LiPF<sub>6</sub>+EC:DEC/LiFePO<sub>4</sub>

**BARRIERS:** Electrode impedance that limits power density and cycle life

**OBJECTIVES:** Improve battery power and life through novel electrode structures. Increase understanding of how electrode morphology influences performance. Develop tools to analyze high-rate performance of electrolytes.

**APPROACH:** We will explore methods for maximizing the high-power performance of low-cost LiFePO<sub>4</sub> composite cathodes. Our efforts will include the use of a variety of electronically conductive additives in order to improve high-rate performance and diminish capacity fade due to loss of conductivity/connectivity. Electrode structure will also be optimized to enhance performance. In addition, as part of our efforts to optimize electronic and ionic conduction in composite electrodes, we will conduct Hall-effect experiments and molecular dynamics (MD) simulations in order to determine transport properties for liquid electrolytes.

**STATUS OCT. 1, 2004:** This will be our first month of the new project. We will acquire the materials required to begin fabrication and testing of LiFePO<sub>4</sub> cathodes. Initial efforts will also include work on the construction of an apparatus for Hall-effect experiments. An improved set of *ab initio* based potentials for MD simulations will be developed.

**EXPECTED STATUS SEPT. 30, 2005:** We will have demonstrated the power and cycle-life improvements possible with different types of electronically conductive additives in LiFePO<sub>4</sub> cathodes, and identified the factors that limit performance. Processing steps for the mixing and application of improved cathode slurries will also have been demonstrated. We will have shown proof-of-concept results for obtaining the electrolyte transference number using the Hall Effect. MD simulations of the transport properties of LiPF<sub>6</sub> in liquid carbonate electrolytes, as a function of temperature and concentration, will be completed.

**RELEVANT USABC GOALS:** HEV-related goals of 30  $\Omega\text{-cm}^2$  impedance and 300k cycles

### MILESTONES:

- (a) Demonstrate that Hall Effect can be used to measure transference numbers. (Apr. 2005)
- (b) Complete initial investigation toward optimizing LiFePO<sub>4</sub> cathode. (Aug. 2005)



## PROGRESS TOWARD MILESTONES

Efforts in the past quarter included fabrication and preliminary testing of  $\text{LiFePO}_4$  cathodes containing new combinations of conductive carbons, in particular carbon fibers, and the continued training of two new graduate students. The ongoing development of experimental and computer-simulation techniques to investigate liquid electrolyte transport properties was also continued this quarter under BATT funding. These investigations will better enable us to overcome the bottlenecks to high-power-density and inexpensive Li rechargeable batteries.

As highlighted here, we fabricated and tested cells utilizing carbon-coated  $\text{LiFePO}_4$  active material (supplied by Hydro-Québec) in the cathode and having a Li counter electrode. The cathode slurries contained a total of 3.5% by weight carbon additives to promote electronic conductivity. The three additives used were graphite (GR), carbon black (CB), and carbon fiber (CF). The vapor-grown carbon fibers, obtained from Pyrograf Products, have diameters in the range 70-200 nm and lengths in the range 50-100  $\mu\text{m}$ .

Assembled cells were tested according to newly prescribed BATT protocols. Shown in Fig. 1 are preliminary results for three cells of different conductivity-additive compositions: one containing only carbon fiber, one containing only graphite and carbon black, and one containing a mixture of the three types of carbon. Before discussing the results, we note that each of the curves represents data from a single cell, and that the reproducibility of the results is currently being established. Furthermore, as indicated on the plot, the respective cathodes differed in thickness; we are currently working toward better control of electrode thickness so we can compare cells having similar thicknesses in the future. Control during the casting process is made especially difficult with fibers present in the cathode slurry.

As depicted in Fig. 1, the discharge capacity at low discharge rates for a standard cathode (graphite + carbon black) was about 82% of theoretical, while that for the carbon-fiber-only cathode was approximately 70%. The best performance of 87% of theoretical capacity was observed for the mixture of carbon particles and fibers. At high discharge rates both cathodes containing carbon fiber performed better than the standard cathode, despite greater thicknesses that adversely affect performance under the metric of percent of theoretical capacity.

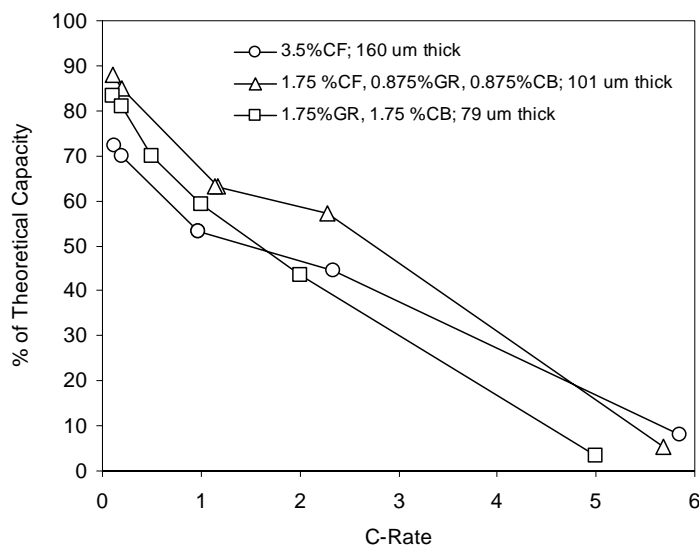


Figure 1. Capacity vs. discharge rate for three cells of varying conductive-carbon compositions and thicknesses as given.

## BATT TASK 2 ANODES

### TASK STATUS REPORT

**PI, INSTITUTION:** M. Thackeray, Argonne National Laboratory

**TASK TITLE:** Anodes - Non-Carbonaceous Materials

**SYSTEMS:** Graphite/LiPF<sub>6</sub>+EC:DEC/LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>  
Graphite/LiBOB+γBL:EA/LiMn<sub>2</sub>O<sub>4</sub>

**BARRIER:** Cost, low temperature and abuse tolerance limitations of Li-ion batteries

**OBJECTIVES:** To replace graphite with an alternative inexpensive anode material that will be compatible, in particular, with low-cost manganese oxide cathodes. The project addresses the need to improve irreversible capacity losses of intermetallic electrodes as well as the low-temperature operation and abuse tolerance of Li-ion cells.

**APPROACH:** Our approach over the past few years has been to search for inexpensive intermetallic electrodes (primarily for EV applications) that provide an electrochemical potential a few hundred mV above the potential of metallic Li, and a capacity of 300 mAh/g and ~2000 mAh/ml. We will focus on: 1) matrix reactions that, when combined with insertion reactions, may have a stronger chance of success than when topotactic reactions are used alone; 2) composite electrodes with Al, Si, Sn, and Sb components to determine their rate capability; 3) pre-lithiation reactions to fabricate charged electrodes for use against non-lithiated metal oxide electrodes and to overcome first-cycle irreversible capacity loss; 4) low-potential metal oxide negative electrodes coupled with the high-potential layered and spinel cathodes of Task 4.1 to yield high-rate and abuse-tolerant Li-ion cells (>3 V) for HEV applications.

**STATUS OCT. 1, 2004:** Composite electrodes containing graphite and a metal component such as Sn or Sb delivered the targeted capacity milestone of 300 mAh/g for 100 cycles. Although in some instances an irreversible capacity loss <20% was achieved on the first cycle, this capacity loss was still a limiting parameter in most cells. Efforts to find a high-performance, low-potential (<1 V vs. Li<sup>0</sup>) metal oxide anode were unsuccessful. Several Li<sub>1+y</sub>MX<sub>2</sub> reactions (*e.g.*, M=V, Mn, Ni, Co) were modeled by *ab initio* calculations; theoretical predictions were verified by experimental observations. Studies of SEI layers on intermetallic electrodes were in progress.

**EXPECTED STATUS SEPT. 30, 2005:** The low-temperature behavior and rate capability of carbon/metal (intermetallic) electrodes will have been determined. The first-cycle irreversible capacity loss of the electrodes and their capacity retention upon cycling will have been improved.

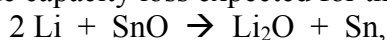
**RELEVANT USABC GOALS:** 10 year life, <20% fade over a 10-year period.

**MILESTONES:** By September 2005: 1) Carbon/intermetallic electrodes: 5-15% irreversible capacity fade on initial cycle; 300 mAh/g for more than 100 cycles; low-temperature rate capability determined. 2) Prelithiated carbon/intermetallic/metal oxide electrodes: synthesized and evaluated electrochemically; 3) Metal oxide electrodes: electrochemical evaluation against high-potential layered and spinel electrodes in >3 V Li-ion cells.

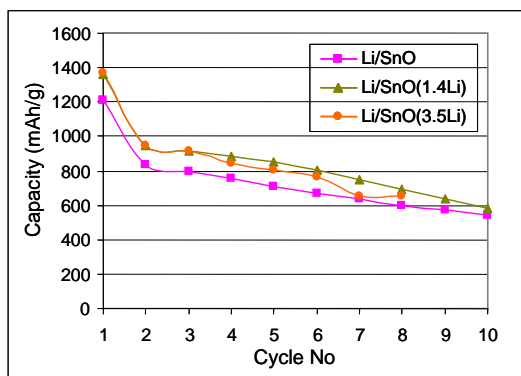
## PROGRESS TOWARD MILESTONES

We are investigating, in collaboration with FMC Corporation, the utility of a Li metal powder product (Lectro<sup>TM</sup> Max Powder) which is stabilized by a surface coating of lithium carbonate. The coating significantly increases the air stability of the powder allowing it to be used in a lamination process. FMC, in collaboration with AEA Technologies in the UK, has already demonstrated the effectiveness of the powder by using it to pre-lithiate graphite anodes when fabricating charged  $\text{Li}_x\text{C}_6/\text{LiV}_3\text{O}_8$  and  $\text{Li}_x\text{C}_6/\text{MnO}_2$  Li-ion cells. We are currently evaluating this powder as a prelithiation agent for non-graphitic anodes such as intermetallic  $\text{Cu}_6\text{Sn}_5$  and the crystalline metal oxides  $\text{SnO}$  and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ . The purpose is: 1) to determine the extent to which the powder can reduce the first-cycle irreversible capacity loss (ICL) at negative electrodes, and 2) to evaluate the differences between reactions of Lectro<sup>TM</sup> Max Powder with insertion compounds (*e.g.*, graphite and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) and with compounds that operate by displacement reactions (*e.g.*,  $\text{SnO}$  and  $\text{Cu}_6\text{Sn}_5$ ). A major advantage of using Lectro<sup>TM</sup> Max Powder is that the amount of Li to be added to the electrode can be accurately controlled.

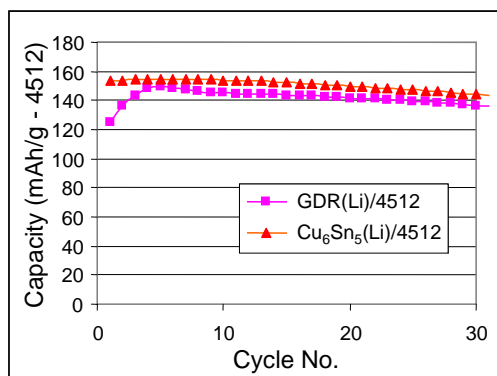
Electrode laminates of  $\text{SnO}$  were pre-made; thereafter, various amounts of Lectro<sup>TM</sup> Max Powder were added to the electrode surface prior to calendaring. There was little evidence that the  $\text{SnO}$  was reduced by this process or by the addition of electrolyte, as reflected by the OCV of fresh cells (2.2 V vs. Li). The irreversible capacity loss expected for the reaction:



which occurs before the formation of  $\text{Li}_4\text{Sn}$ , is 33%. This was confirmed by the initial discharge-charge reaction of  $\text{Li}/\text{SnO}$  cells. The addition of Lectro<sup>TM</sup> Max Powder, for both 1.4 and 3.5  $\text{Li}/\text{SnO}$ , increased the first-cycle capacity but did not significantly reduce the ICL (Fig. 1).



**Figure 1.** Capacity vs. Cycle No.:  $\text{Li}/\text{SnO}$  cells



**Figure 2.** Capacity vs. Cycle No.:  $\text{C}/\text{Li}_4\text{Ti}_5\text{O}_{12}$  and  $\text{Cu}_6\text{Sn}_5/\text{Li}_4\text{Ti}_5\text{O}_{12}$  cells

Lithium-ion cells with the configuration  $\text{C}(\text{GDR})/\text{Li}_4\text{Ti}_5\text{O}_{12}(4512)$  and  $\text{Cu}_6\text{Sn}_5/\text{Li}_4\text{Ti}_5\text{O}_{12}$ , in which Lectro<sup>TM</sup> Max Powder was used to prelithiate the GDR graphite and  $\text{Cu}_6\text{Sn}_5$  electrodes, were also evaluated. In both instances, good cycling stability was achieved for the initial 30 cycles, the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  electrode yielding 140-150  $\text{mAh/g}$  at a C/10 rate, *i.e.*, ~80% of its theoretical capacity (175  $\text{mAh/g}$ ) (Fig. 2). Our conclusion from these preliminary studies is that Lectro<sup>TM</sup> Max Powder is effective for prelithiating insertion electrodes such as electronically-conducting graphite that can react immediately to form  $\text{Li}_x\text{C}_6$ , whereas electrodes that operate by displacement reactions, such as  $\text{SnO}$  and  $\text{Cu}_6\text{Sn}_5$ , may not react readily with the powder, presumably as a result of insulating surface layers, reaction kinetics and activation barriers, and particle size restrictions that prevent the prelithiation reactions from proceeding to completion.

## TASK STATUS REPORT

**PI, INSTITUTION:** M.S. Whittingham, SUNY at Binghamton

**TASK TITLE - PROJECT:** Anodes - Novel Materials

**SYSTEMS:** Li-Ion: all systems

**BARRIER:** Cost, safety and volumetric capacity limitations of Li-ion batteries

**OBJECTIVES:** To replace the presently used carbon anodes with safer materials that will be compatible with low-cost manganese oxide and phosphate cathodes and the associated electrolyte.

**APPROACH:** Our anode approach is to explore, synthesize, characterize and develop inexpensive materials that have a potential about 500 mV above that of pure Li (to minimize risk of Li plating and thus enhance safety) and have higher volumetric energy densities than carbon. We will place emphasis on simple metal alloys/composites, and on intercalating oxides. All materials will be evaluated electrochemically in a variety of cell configurations, and for thermal and kinetic stability.

**STATUS OCT. 1, 2004:** We have shown that vanadium and manganese oxides, in their highest oxidation states, are not prime candidates. Pure Al foil and expanded metal were found to have high capacities and react readily with Li, but its capacities faded rapidly upon cycling in carbonate-based electrolytes; Al-based alloys show behavior inferior to pure Al. Tin-containing materials, such as  $\text{MnSn}_2$ , cycle well for a few cycles before capacity fade sets in. Pure tin-foil anodes cycle better than pure Al or  $\text{MnSn}_2$ , but the cell impedance was found to increase markedly after about ten cycles; an expanded tin grid was marginally superior, but not sufficient to justify further study.

**EXPECTED STATUS SEPT. 30, 2005:** From our program to understand capacity fade of tin upon cycling, we expect to have defined the key parameters determining capacity loss, to have determined the impact of tin morphology on capacity fade, and as a result to have identified several additional non-Al binary alloys; and to have improved the electrochemical performance of the materials identified.

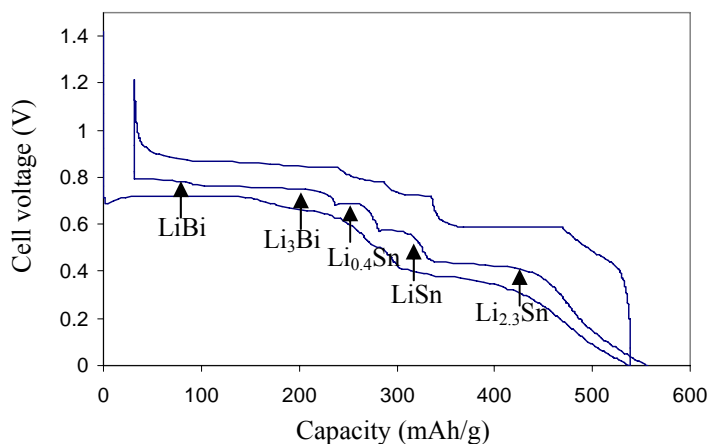
**RELEVANT USABC GOALS:** 300,000 shallow discharge cycles, and abuse tolerance to cell overcharge and short circuit.

**MILESTONES:** (a) We will design a program to identify, understand, and mitigate the capacity loss upon cycling of simple alloy systems. This will result in a milestone to understand and define the key parameters determining capacity fade in pure tin and its alloys by June 2005, and to propose a means of remediating that fade. (b) We will identify the impact of electrolyte solvent and salt on the capacity retention and rate capability of pure tin, including first-cycle capacity loss, by October 2005.

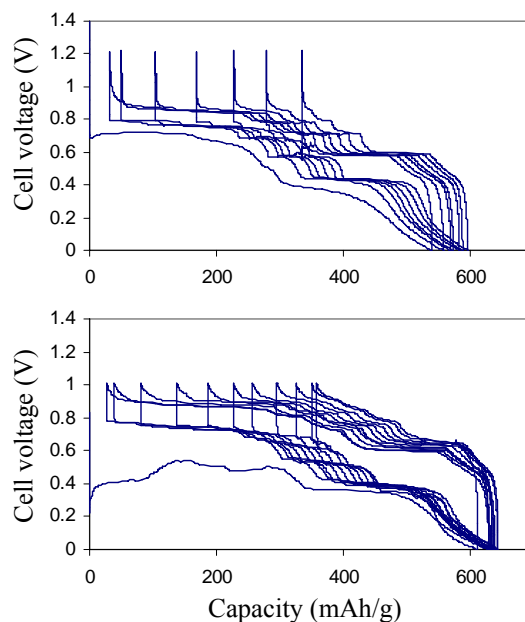
## PROGRESS TOWARD MILESTONES

In the previous report we reported the electrochemistry of tin foil mounted on copper, which was inferior to tin foil itself. In this quarter, we have expanded on our studies of two reacting phases, the Sn-Bi system, and are exploring manganese oxides as anodes.

The bismuth-tin eutectic alloy (Bi:Sn = 58:42 wt%) was mechanically rolled into a 30-40  $\mu\text{m}$  thick foil. Figure 1 shows the initial 3 sweeps at 1  $\text{mA}/\text{cm}^2$ . The capacity reached about 550  $\text{mAh}/\text{g}$ , according to  $\text{Li}_{3.5}(\text{Sn-Bi})$ . After the first rather featureless Li intercalation, five plateaus show in the following recharge and discharge processes. These five plateaus correspond to  $\text{Li}_1\text{Bi}$ ,  $\text{Li}_3\text{Bi}$ ,  $\text{Li}_{0.4}\text{Sn}$ ,  $\text{Li}_1\text{Sn}$ ,  $\text{Li}_{2.3}\text{Sn}$  respectively, clearly showing that both tin and bismuth participate. Figure 2 compares the cycling behavior of the Sn-Bi foil in Swagelok and coin cells at the same current density. The coin cell has a slightly higher initial capacity (~640  $\text{mAh}/\text{g}$ ), and less irreversible capacity loss (which is 25  $\text{mAh}/\text{g}$  for coin cell and 31  $\text{mAh}/\text{g}$  for Swagelok). The coin cell also maintains its capacity slightly better, which may be associated with the greater pressure maintained across the cell during cycling. Both cells, however, show unacceptable capacity loss during cycling. We will explore their behavior in LiBOB salt based electrolytes.



**Figure 1.** Cycling of Sn-Bi eutectic foil in Swagelok cell at 1  $\text{mA}/\text{cm}^2$ .



**Figure 2.** Cycling of Sn-Bi eutectic foil upper: in Swagelok cell; lower: in coin cell.

We have investigated the anodic behavior of some mixed manganese-vanadium oxides in the past, and are expanding that study to manganese oxides based on the promising results presented by the Amiens group of Tarascon on  $\text{CoO}$ . Specifically we are exploring forming nanosized fibers of  $\text{MnO}_x$ , and will compare them to the titanium oxide spinel anode.

**Further plans to meet or exceed milestones:** None

**Reason for changes from original milestones:** No changes

### Publication

Quan Fan, Peter Zavalij, and M. Stanley Whittingham, "Anode Hosts for Lithium Batteries: Revisiting Tin and Aluminum," *Mater. Res. Soc. Proc.*, **835**, K6.16 (2005).

## TASK STATUS REPORT

**PI, INSTITUTION:** G.A. Nazri and D. Curtis, University of Michigan  
T. Malinski, Ohio University

**TASK TITLE - PROJECT:** Anodes – Novel Composite Anodes for Lithium-ion Batteries

**SYSTEMS:** Low-cost Li-ion battery, improved safety, long cycle and calendar life

**BARRIERS:** Poor cycle life, poor safety, self-discharge, and electrolyte decomposition

**OBJECTIVES:** Develop a low-cost and safe composite anode with no intrinsic irreversible capacity loss (ICL) and with higher gravimetric and volumetric energy density than the current carbonaceous anodes. Improve the kinetics of the Li insertion-extraction process in the composite anodes for application in high-power Li-ion cells.

**APPROACH:** Prepare alternative composite anodes *via* reactive mechano-milling of anode materials with lithium or lithium hydride to eliminate the inherent irreversible capacity loss of metal-oxide anodes. Form a desirable synthetic SEI layer *via* the mechano-reduction of oxide anodes in presence of electrolyte, and improve the kinetics of the Li insertion - extraction process by optimization of anode particle size to nanoscale.

**STATUS OCT. 1, 2004:** The optimization of mechano-milling process parameters for reactive reduction of metal oxide, nitride, and phosphides anodes will be completed. The chemical nature of the SEI formed on metals and alloys after due to reduction of their oxides, nitrides, and phosphides will be completed. An electrochemical study of the composite anode in baseline electrolyte (EC-DMC containing 1 M LiPF<sub>6</sub>) will be studied.

**EXPECTED STATUS SEPT. 30, 2005:** Final report will be submitted.

**RELEVANT USABC GOALS:** Exceeding 10-year life, high power battery electrode, low cost battery and high safety

**MILESTONES:** Final report will be submitted by June 30, 2005.

## **BATT TASK 3 ELECTROLYTES**

### **TASK STATUS REPORT**

**PI, INSTITUTION:** N.P. Balsara, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Development and Polymer Electrolytes and Gels for Advanced Lithium Batteries

**SYSTEMS:** Nanostructured polymer electrolytes based on polystyrene-polyethyleneoxide (PS-PEO) block copolymers. End crosslinked PEO swollen with EC:DEC mixtures.

**BARRIERS:** Poor electrolyte transport and low power, particularly at low temperatures, short life due to power and capacity fade.

**OBJECTIVES:**

- Obtain PS-PEO diblock copolymer films with maximum ionic conductivity.
- Study the stability of PS-PEO electrolytes against Li electrodes.
- Develop and characterize the properties of uniformly crosslinked PEO gels swollen with EC:DEC mixtures.

**APPROACH:** To synthesize and characterize new polymeric electrolytes. This includes gel electrolytes and nanostructured dry polymer electrolytes. Polymers will be characterized by methods such as neutron scattering, dielectric relaxation spectroscopy, rheology and light scattering to obtain new insights into the rate-limiting transport processes. The materials will be tested for stability against Li electrodes.

**STATUS OCT. 1, 2004:** Rheological properties of PEO/LiTFSI and polytetramethyleneoxide/LiTFSI (PTMO/LiTFSI) mixtures have been measured and analyzed. Polystyrene-polyethyleneoxide (PS-PEO) block copolymers will be synthesized. Low cost synthetic routes for uniformly crosslinked polymer gel electrolytes will be established. The relevant mechanical and electrical properties of the electrolytes will be measured.

**EXPECTED STATUS SEPT. 30, 2005:** Synthesis and characterization of a new class of gel electrolytes with uniform crosslinking density. Completion of structural and conductivity measurements on the gel electrolytes. Characterization of nanostructured PS-PEO electrolytes including tests of stability against Li electrodes. We will continue collaborating with John Kerr and other members of the BATT program on the thermodynamic and rheological characterization of polymer gel electrolytes.

**RELEVANT USABC GOALS:** 30 ohm-cm<sup>2</sup> area-specific impedance, cold cranking capability to -30°C, 300,000 shallow discharge cycles, abuse tolerance to cell overcharge and short circuit.

**MILESTONES:**

1. To measure conductivity, mechanical properties, and stability against Li electrodes of dry, nanostructured PS-PEO-based electrolytes. (Sept. 2005)
2. Synthesize and characterize uniformly crosslinked PEO systems for gel polymer electrolytes applications. (Sept. 2005)

## PROGRESS TOWARD MILESTONES

### 1. Nanostructured Polymer Electrolytes.

We have measured the electrical, mechanical, and morphological characteristics of a series of a poly(styrene-block-ethylene oxide) diblock copolymer (PS-b-PEO) systems. Characterization tools used include small angle X-ray scattering (SAXS), transmission electron microscopy (TEM), optical birefringence, and rheology. LiTFSI, was added to each sample (at an [EO]/[Li] ratio of 50) for ionic conductivity. Each sample was pressed into 1-mm thick pellets, and all sample preparation steps were conducted in a dry box. AC impedance measurements were made on these polymer electrolyte membranes to obtain the bulk ionic conductivity. Results indicate that conductivity values are approximately a quarter that of pure PEO with the same salt concentration and temperature. The conductivity results are very promising with values on the order of  $10^{-5}$  S/cm at 80°C. Below 60°C, PEO domains remain crystalline in the diblock copolymer. We have investigated the effect of addition of the salt (LiTFSI) on the crystallinity of the PEO domains. We are very encouraged to find out that the salt acts as a plasticizer in the PS-b-PEO as well. The crystallization of the PEO domains is suppressed at room temperature at a salt concentration corresponding to an [EO]/[Li] ratio of 15. We are currently in the process of measuring the conductivity of these samples at room temperature. The mechanical property of this polymer electrolyte system does not change much with the temperature below the glass temperature of polystyrene domains (~90°C). At 80°C, preliminary indications are that the modulus of this material exceeds the upper limit of our current rheometer (which is at least  $10^8$  Pa). We have also started testing these membranes with Li electrodes (in Swagelok cells) with the help of Gao Liu and Yong Bong Han. We are currently working on improving the electrode-membrane contact to reduce the interfacial impedance.

### 2. Polymer Gel Electrolytes.

We have made some progress in our work on the polymer electrolyte gel system. We have synthesized crosslinked poly (acrylamidomethylpropanesulfonic acid) gels using free radical polymerization (50°C) facilitated by ammonium persulfate (APS) as redox initiator. We have been able to replace  $H^+$  by  $Li^+$  by neutralizing the monomer with  $Li_2CO_3$ . This allows us to synthesize poly(AMPSA-  $Li^+$ ) gels that can serve as single ion gel conductors. Since, this reaction can be carried out in the presence gel electrolytes at 50°C, the monomer solution (AMSA-  $Li^+$ ) solution in EC/PC/DEC can be gelled in between the electrodes. We will monitor the crosslinking density to control the rheological properties of the poly(AMPSA). We are also investigating the possibility of using this polymer gel system with ionic liquids. We will be working with Justin Salminen on testing the poly(AMPSA-  $Li^+$ ) gels with a range of ionic liquids.



## TASK STATUS REPORT

**PI, INSTITUTION:** J. Kerr, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Electrolytes - R&D for Advanced Lithium Batteries

**SYSTEMS:** High-voltage, high-energy: Gr/LiPF<sub>6</sub>+EC:DEC/LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>  
Low-voltage, high-stability: Gr/LiPF<sub>6</sub>+EC:DEC/LiFePO<sub>4</sub>  
High-voltage, high-power: Gr/LiBOB+γBL:EA/LiMn<sub>2</sub>O<sub>4</sub>

**BARRIERS:** Poor electrolyte transport and low power, particularly at low temperatures, short life due to power and capacity fade, low abuse tolerance.

### OBJECTIVES:

- Determine and quantify the improvement (if any) in abuse tolerance of polymer gel electrolytes over liquid electrolytes.
- Determine the limitations on Li-ion transport in polymer gel electrolytes and the electrolyte component of composite electrodes and develop materials capable of high-power operation at ambient temperature with lithiated carbons/Li metal alloy anodes and high-voltage cathode materials.
- Determine the feasibility of the use of Li metal electrodes with polymer gel electrolytes and provide operating conditions that prevent dendrite growth and high coulombic efficiencies at HEV rates.

**APPROACH:** A physical organic chemistry approach is taken to electrolyte design, thereby ensuring that not only are the sources of poor performance and failure pinpointed but also the problem can be corrected through materials design and synthesis.

**STATUS OCT. 1, 2004:** Characterization of mechanical, transport, electrochemical, and chemical properties of cross-linked comb-branch and linear polymers and polyelectrolytes will be completed for both dry polymer electrolyte used with Li metal and polymer gel electrolytes with carbon. Modifications of Li metal surfaces and conducting carbon particles will be assessed.

**EXPECTED STATUS SEPT. 30, 2005:** State-of-the-art polymers will be procured or synthesized to prepare polymer gel electrolytes with the base system electrolyte components. The effects of the gel on abuse tolerance and transport properties will be determined. The performance of single-ion conductor gels will be compared with the binary systems. Compatibility of the polymer electrolyte and polyelectrolyte gels with Li metal and Li alloy electrodes will also be explored.

**RELEVANT USABC GOALS:** 15 year life, <23% power fade, specific power 625 W/kg at the system level.

### MILESTONES:

- 1) Demonstrate and quantify the change in abuse tolerance resulting from use of gel polymer electrolytes relative to liquid electrolytes in the three cell systems. (Sept. 2005)
- 2) Quantify the effect of gel polymer electrolytes on transport properties relative to liquid electrolytes. (Sept. 2005)

## PROGRESS TOWARD MILESTONES

### 1. Abuse Tolerance of Gel Electrolytes.

The chemical reactions of ethylene oxide based polymers and solvent components (EC, EMC) with Lewis acid salts ( $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiBOB}$ ) have been further investigated using GC/MS, GPC and CE in addition to cell cycling with Li metal symmetrical cells. Comb-branch polymer electrolytes based on ethylene oxide units combined with a wide variety of Li salts were cycled with Li metal for extended periods.  $\text{LiTFSI}$  and  $\text{LiBETI}$  could be cycled indefinitely with no sign of dendrite formation. The Lewis acid salts behaved very poorly in comparison. Even  $\text{LiBOB}$  showed signs of reaction. Post-mortem GC analysis of the cycled cells showed little or no reaction with the well-behaved salts but many reaction products for the Lewis acid salts. Control reactions with electrolytes sealed in cells in contact with Li metal and with stainless steel electrodes showed that the products were formed with the Lewis acid salts regardless of the presence of the electrodes. The Lewis acid salts are inherently reactive with ethylene oxide based polyethers.

Recently it has been reported that  $\text{LiPF}_6$  in EC or PC shows no sign of reaction in a TGA experiment. This is consistent with our report of a stable adduct between  $\text{PF}_5$  and EC that was detected by GC/MS. These results contradict previous results that reported reaction of EC with Lewis acid salts in Li-ion electrolytes. It has now been observed that  $\text{LiF}$  is apparently quite soluble in pure EC and PC but insoluble in linear carbonates such as DMC, EMC, etc. The reactivity of  $\text{LiPF}_6$  in Li-ion electrolytes will depend on the solubility of  $\text{LiF}$ .  $\text{LiPF}_6$  is completely stable in water as the  $\text{LiF}$  is soluble. In cases where the  $\text{LiF}$  precipitates the  $\text{PF}_5$  is sufficiently long-lived to react in another fashion such as on the EC or on PEO ether chains. These observations may rationalize some long-standing puzzles such the unique behavior of EC in Li-ion batteries. More detailed studies of these reactions are underway.

### 2. Transport Properties.

Transport property measurements of  $\text{LiTFSI}$ -PTMO and  $\text{LiBETI}$ -PTMO have been carried out. The concentration cell data for the  $\text{LiTFSI}$  system show a much smaller variation in potential with concentration than with PEO. This is consistent with the lower dielectric constant of the TMO system. These experiments are carried out to complete work on dry Li/polymer systems as well as provide a comparison for the gel systems that will be prepared by addition of solvent components to the crosslinked polymers.

### 3. Dendrite Initiation in Li Polymer cells.

A model for dendrite initiation has been formulated that takes into account the plastic deformation of Li metal. This model provides an explanation for the effect of external pressure and indicates that an elastic modulus of  $5 \times 10^7$  Pa for the cross-linked polymer is sufficient to kinetically inhibit dendrite initiation. Experiments to verify the model have been initiated and it has been noted that the interfacial impedance also has a strong effect.

## TASK STATUS REPORT

**PI, INSTITUTION:** S.A. Khan, P.S. Fedkiw, North Carolina State University;  
G.L. Baker, Michigan State University

**TASK TITLE - PROJECT:** Electrolytes - Composite Polymer Electrolytes for Lithium and Lithium-Ion Batteries

**SYSTEMS:** Low-cost composite polymer/gel electrolytes

**BARRIER:** Short lithium battery lifetimes and high costs.

**OBJECTIVES:** The ultimate objectives are to develop composite polymer/gel electrolytes that are low cost, have high conductivities, impart electrode-electrolyte interfacial stability, and yield long cycle life.

**APPROACH:** Our approach is to use surface-functionalized fumed silica fillers in BATT-baseline and candidate systems to determine the effects of filler type and concentration on interfacial stability and cell cycling. We correlate these electrochemical characteristics with mechanical properties and materials chemistry (*e.g.*, silica-type or PEO-type, synthesized by Baker or Kerr, respectively). Data collected include elastic and viscous moduli, ionic conductivity, transference number, Li cycling efficiency, Li-electrolyte interfacial resistance, and full-cell cycling capacity using 4-V cathodes.

**STATUS OCT. 1, 2004:** We have established that fumed silica-based composite electrolytes with low-molecular weight (MW) PEOs exhibit desirable mechanical properties characteristic of solid electrolytes (*e.g.*, elastic modulus  $G' > 10^5$  Pa), yet have the processability of liquids and display conductivities rivaling liquid electrolytes ( $\approx 10^{-3}$  S/cm at 25°C). Fumed silica stabilizes the Li/electrolyte interface, effectively suppresses Li dendrite growth, and attenuates Al corrosion in presence of LiTFSI. We have found that addition of fumed silicas into low-MW PEOs significantly improves charge-discharge cycle performance, coulombic and energy efficiencies, rate capabilities, and self-discharge performance of Li/V<sub>6</sub>O<sub>13</sub> cells. We have further determined that adding fumed silica improves the rheological properties of both high-MW and mixed-MW polymer electrolytes, but can be either beneficial or detrimental to ion-transport behavior. In this regard, adding fumed silica also improves the interfacial stability of the Li/electrolyte (both high-MW and mixed-MW PEO) interface and cycle performance of Li/V<sub>6</sub>O<sub>13</sub> cells. We have also synthesized single-ion conducting fumed silica [Degussa R711-poly(lithium 2-acrylamido-2-methyl-1-propanesulfonate), R711-pLiAMPS.]

**EXPECTED STATUS SEPT. 30, 2005:** We expand the scope of our work to explore effects of adding fumed silica into BATT baseline electrolytes for Li-ion systems including rheological and transport properties, and interfacial stabilities. We will also examine Li/electrolyte interfacial stability and rheology of electrolytes consisting of mixtures of Li salt + single-ion conducting fumed silicas as a function of electrolyte composition and salt type.

**RELEVANT USABC GOALS:** Specific power 300 W/kg, 10 year life, < 20% capacity fade.

**MILESTONES:** (a) Investigate effects of adding fumed silica into BATT baseline electrolytes on transport and rheological properties, and interfacial stabilities, with a focus on low-temperature performance. September 2005.

(b) Examine the interfacial stability and rheology of mixtures of Li salt + single-ion conducting fumed silicas in polymer gel solvents as a function of silica concentration and salt type, including new lithium imide salts developed by Drs. DesMarteau and Creager at Clemson. September 2005.

## PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestones over last quarter:**

We continue to explore suitable gel electrolytes for Li-ion batteries based on BATT baseline systems. We have investigated liquid electrolyte 1M LiBETI (3M)/ EC:PC:DMC:DEC (1:1:1:1). Chronoamperometry and linear sweep voltammetry results show that an Al current collector is stable with the above electrolyte up to 5.25 V. Gel electrolytes were blends of 10 wt% fumed silica + 1M LiBETI/ EC:PC:DMC:DEC (1:1:1:1). Three types of fumed silica were employed A200, COX84, and R805 and gel behavior was observed for all; that is, the elastic modulus exceeds the viscous modulus over the frequency range and is independent of the frequency. The fumed silica has a negligible effect on conductivity. Cycling of Li(Ni)/electrolyte/Li cells shows that fumed silica improves the interfacial stability both at room and low temperature (3 ~ 5°C). The cycling efficiency is also improved by adding fumed silica.

We have studied the effect of various Li salts on the ionic transport properties of composite electrolytes containing single-ion conducting fumed silica [Degussa R711-poly(lithium 2-acrylamido-2-methyl-1-propanesulfonate), R711-pLiAMPS, surface  $\text{Li}^+$  content  $\gamma = 4.2 \text{ nm}^{-2}$ ] + PEGdm (Mw = 250, Li:O = 1:20). Four different Li salts were used: lithium bis(trifluoromethylsulfonyl)imide ( $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ , LiTFSI, 3M), lithium bis(perfluoroethylsulfonyl)imide ( $\text{LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2$ , LiBETI, 3M), lithium bis(oxalato)borate ( $\text{LiB}(\text{C}_2\text{O}_4)_2$ , LiBOB, Chemetall), and lithium phosphate ( $\text{Li}_3\text{PO}_4$ , Aldrich). The addition of Li salt greatly improves conductivity, and although the  $\text{Li}^+$  transference number  $t_{\text{Li}^+}$  decreases with salt addition, it remains high relative to electrolyte with Li salt as the sole charge carrier. Among the four salts examined, LiTFSI and LiBOB have a better ability to increase the conductivity and maintain a higher  $t_{\text{Li}^+}$  than LiBETI and  $\text{Li}_3\text{PO}_4$ .

We have evaluated the mechanical properties of mixed-MW polymer electrolytes using PEO/PEGdm(250) blends. The effects of blend ratio as well as fumed silica nanoparticle surface chemistry have been studied. Two different types of particles were employed: hydrophilic A200 and hydrophobic R805. The PEO used in these experiments contains inorganic fillers; therefore a purification step prior to blending was required in order to remove them. Thermogravimetric analysis confirmed the efficiency of our purification protocol. Dynamic rheological experiments revealed that blends of PEO/PEGdm(250) and FS containing up to 20 wt% of the low-MW component exhibit a gel-like behavior within the frequency range studied. As the concentration of the low-MW component increases in blends containing R805, the viscous modulus begins to dominate at lower frequencies, indicating that the material transitions from a gel to viscous liquid. In contrast, blends containing hydrophilic A200 showed this transition at concentrations of PEGdm(250) lower than 20 wt%. Though a decrease of the moduli is observed with the addition of PEGdm(250), this effect is not noticeable when 10 wt% of the low-MW component is added to the blends.

- **Reason for changes from original milestone:** N/A

## TASK STATUS REPORT

**PIs, INSTITUTION:** D. DesMarteau and S. Creager, Clemson University

**TASK TITLE – PROJECT:** Electrolytes - New Battery Electrolytes Based on Lithium Fluorosulfonate and Fluorosulfonimide Salts

**SYSTEMS:** Graphite / LiPF<sub>6</sub>+EC:DEC / LiFePO<sub>4</sub>

**BARRIERS:** Poor electrolyte transport, low power, short life, abuse tolerance.

**OBJECTIVES:** (1) Synthesize new lithium fluorosulfonate and fluorosulfonimide salts for which anion attachment to a suitable plasticizer, scaffold, or matrix can be accomplished; (2) Characterize battery electrolytes made from the target salts with respect to structure, transport properties (conductivity, salt diffusion, transference), reactivity (*e.g.*, with electrode materials and current collectors), and battery performance (power, fade, interface stability).

**APPROACH:** Salts will be synthesized using variants of methods developed at Clemson over the last 15 years (D. DesMarteau, *J. Fluorine Chem.* 1995, **72**, 203-208). Transport properties will be measured using EIS combined with restricted diffusion and potentiostatic and galvanostatic polarization techniques as needed. Reactivity with electrode materials will be studied by calorimetry, and half-cell and full-cell cycle testing will be performed using standard techniques with assistance from and/or in collaboration with other BATT researchers.

**STATUS Oct. 1, 2004:** Oligomeric salts of structure CF<sub>3</sub>SO<sub>2</sub>[N(Li)-SO<sub>2</sub>R<sub>f</sub>SO<sub>2</sub>]<sub>n</sub>N(Li)SO<sub>2</sub>CF<sub>3</sub> were provided to BATT coworkers for half-cell, rheology, and Al corrosion testing. Allyl ether salts of structure CH<sub>2</sub>=CHCH<sub>2</sub>O-CF<sub>2</sub>CFH-OCF<sub>2</sub>CF<sub>2</sub>-salt where salt=SO<sub>3</sub>(Li) and SO<sub>2</sub>N(Li)SO<sub>2</sub>CF<sub>3</sub> were provided to BATT coworker Kerr for use making single-ion conductors. Transport studies on SPEs prepared using oligomeric fluorosulfonimide salts will be completed. Ionic melts of structure PEG-O-CF<sub>2</sub>CHFO-CF<sub>2</sub>CF<sub>2</sub>-salt will have been synthesized and preliminary characterization including conductivity studies completed.

**EXPECTED STATUS SEPT. 30, 2005:** Plasticized electrolytes of general structure (X)-O-CF<sub>2</sub>CHFO-CF<sub>2</sub>CF<sub>2</sub>-salt where salt = SO<sub>3</sub>Li or SO<sub>2</sub>N(Li)SO<sub>2</sub>CF<sub>3</sub> and X = PEG, polyether, polysiloxane, and silica will have been synthesized and characterized with respect to conductivity and reactivity, and samples provided to other BATT workers for further testing.

**RELEVANT FREEDOMCAR GOALS:** 15 year life, <23% power fade, specific power 625 W/kg at the system level.

### MILESTONES:

- (1) Synthesize new electrolytes of general structure X-O-CF<sub>2</sub>CHFO-CF<sub>2</sub>CF<sub>2</sub>-salt where salt = SO<sub>3</sub>Li or SO<sub>2</sub>N(Li)SO<sub>2</sub>CF<sub>3</sub> and X = a PEG oligomer, a comb-branch network polyether, an OH-functionalized siloxane polymer, or a functionalized fumed silica particle. May 05.
- (2) Characterize the resulting electrolytes with respect to structure, transport properties, reactivity with anode and cathode materials, and battery performance using EIS, scanning calorimetry, half-cell and full-cell cycle testing, and other techniques as needed. Sept 05.

## PROGRESS TOWARD MILESTONES:

Substantial progress was made in synthesizing and characterizing ionic melts of structure  $X\text{-OCF}_2\text{CFH-OCF}_2\text{CF}_2\text{-salt}$  where  $X$  = a PEG oligomer and salt =  $\text{SO}_3\text{Li}$  or  $\text{SO}_2\text{N(Li)SO}_2\text{CF}_3$ , which are targeted due to their anticipated favorable combination of high ionic conductivity and lack of salt concentration polarization under high-rate charging and discharging conditions. Work from last quarter was extended to include fluorosulfonimide salts where  $X$  = a PEG monomethyl ether of MW 350 (average of 7.2 ethylene oxide units per chain), and conventional PEG oligomers of MW 1000 and 2000 (22 and 44 ethylene oxide units per chain respectively). The latter two PEG oligomers are salt-functionalized on both ends instead of just one end. Conductivity data were acquired for all materials, with the highest conductivities being realized for the material synthesized last quarter with  $X$  = PEG monomethyl ether of MW 550 (avg. of 11.8 ethylene oxide units per chain) and salt =  $\text{SO}_2\text{N(Li)SO}_2\text{CF}_3$ . It is thought that this material provides the optimal combination of Li dissociation, melt viscosity, and EO:Li ratio to achieve high conductivity. Comparisons of conductivity data with recent results from modeling studies on similar materials performed by BATT co-worker Smith have been revealing, and will be pursued in greater depth to help improve understanding of the factors affecting Li transport in polyether-based ionic melts. Thermoanalytical studies on these materials were also initiated this quarter. Preliminary DSC results on several fluorosulfonimide-derivatized PEG materials showed glass transitions near  $-40^\circ\text{C}$  but no melting / freezing transitions between  $-130$  and  $+150^\circ\text{C}$ . This is in contrast to the unmodified PEG monomethyl ether (MW 550) which melts (freezes) near  $+15^\circ\text{C}$ . Options for performing calorimetry on mixtures of electrolytes with anode and cathode materials to assess battery safety are being explored.

Work aimed at scaling up the synthesis of ionic melt materials to produce amounts adequate for cycle testing and for rheology and further reactivity testing has begun. A special effort is required to keep the entire reaction mixture cool, since the reactions involved are highly exothermic and prior project work has showed that warm conditions can result in production of undesired side products. Initial attempts at scale-up have failed due to difficulties in dissipating the reaction heat when performing reactions on a large scale. A reaction vessel with integrated internal cooling coils is being constructed and will be used to solve this problem.

Other work from this quarter includes: successful synthesis of a bis-trifluorovinyl ether salt of structure  $\text{CF}_2=\text{CFO-CF}_2\text{CF}_2\text{-SO}_2\text{N(Li)SO}_2\text{-(CF}_2)_4\text{-SO}_2\text{N(Li)SO}_2\text{-CF}_2\text{CF}_2\text{-OCF}=\text{CF}_2$  suitable for making ionic melts of structure PEG-salt-PEG; and continued studies of alternate coupling reactions involving fluorosulfonimides functionalized with aryl diazonium and aryl iodide groups. Attachment of these latter salts onto polyethers is expected to be especially favored and facile. Attempts to polymerize the lithium fluorosulfonimide epoxide salt of structure  $\text{CH}_2\text{OCHCH}_2\text{-OCF}_2\text{CFH-OCF}_2\text{CF}_2\text{-SO}_2\text{N(Li)SO}_2\text{CF}_3$  which was synthesized last quarter have so far been unsuccessful; however alternate approaches to using this molecule to make battery electrolytes are being explored. Finally, transference number measurements on SPEs fabricated using fluorosulfonimide oligomer Li salts from the project were completed via collaboration with BATT coworkers Fedkiw and Kahn at NCSU. A promising trend toward higher Li transference for salts of the larger oligomers is evident, although the increases in Li transference are fairly modest (*e.g.*, increase in  $t_+$  from 0.31 for LiTFSI to 0.48 for a 24-anion oligomer salt) and probably not sufficient to have a large impact on battery performance.

## TASK STATUS REPORT

**PI, INSTITUTION:** G.D. Smith and O. Borodin, University of Utah

**TASK TITLE - PROJECT:** Electrolytes - Molecular Modeling of Solid Polymer Electrolytes, Single Ion Conductors and Gel Electrolytes

**SYSTEMS:** Low -cost Li-ion

**BARRIERS:** Poor cation transport properties of gel electrolytes at ambient temperatures. Poor transport through SEI layer and poor chemical stability of the SEI layer.

**OBJECTIVES:** Gain molecular level understanding of the cation transport mechanism in single-ion conductor gel electrolytes. Develop new single ion conductor gel electrolytes with improved ion transport and mechanical properties. Understand Li transport in the SEI layer at the SEI layer/electrolyte interface.

**APPROACH:** Perform virtual synthesis and detailed characterization of a number of single-ion conductor electrolytes. Vary the structure of the single-ion conductor and the fraction of the plasticizer (ethylene carbonate, or EC) in gel electrolytes in order to optimize the ion transport and mechanical properties of polymer electrolytes. Perform MD simulations of the SEI layer and SEI/electrolyte interface to predict structural properties and Li transport of these battery components.

**STATUS OCT. 1, 2004:** Molecular dynamics (MD) simulations have been carried out on a number of single-ion conductors based on polyether type comb-branched polymers with TFSI<sup>-</sup> anions attached to side chains and ionic liquids with the structure LiTFSI-EO<sub>n</sub>-TFSILi as a function of temperature. The length of side chains, the Li<sup>+</sup> cation concentration, and the concentration of EC will be varied in order to determine the structure with the best ion transport parameters. Temperature dependence of the transport properties of gel electrolytes will be investigated at one concentration of plasticizer.

**EXPECTED STATUS SEPT. 30, 2005:** A detailed study of the influence of comb-branched copolymer architecture and plasticizer concentration on structural and transport properties of single-ion conductor gel electrolytes as a function of temperature will be investigated for the following parameters: the length of side chains and their spacing, salt concentration, and amount of plasticizer. The structure of the alkyl carbonate component of the anode SEI layer will be predicted. Lithium transport in the SEI layer components and at the interface of the SEI with the gel electrolyte will be studied on the molecular level using MD simulations.

**RELEVANT USABC GOALS:** Specific power 300 W/kg, 10 year life, < 20% capacity fade

**MILESTONES:** 1) Complete investigation of the effect of the length of side chains, salt concentration and EC concentration on structural and transport properties of single-ion conductor gel electrolytes at three temperatures. (June 1, 2005)  
2) Finish investigation of the anode SEI layer structure, Li transport, and interface with the gel electrolytes. (Sept. 2005)

## PROGRESS TOWARD MILESTONES

Over the last quarter we continued molecular dynamics (MD) simulations of a number of ionic liquids with the structure  $\text{LiTFSI}-(\text{EO})_n-\text{LiTFSI}$   $n=12, 20, 40$ ; gel and dry single-ion conductors of various architectures with the (trifluoromethanesulfonyl) imide anion immobilized on the comb-branched polymer-host side chains with and without EC plasticizer added. MD simulations of gel electrolyte consisting of (trifluoromethanesulfonyl) imide anion immobilized on the comb-branched polymer-host side chain plasticized with pentaglyme have been initiated. We expect that changing the plasticizer from EC used in our previous simulations to the pentaglyme would lead to a larger fraction of the  $\text{Li}^+$  cations complexed by the plasticizer and not by the polyelectrolyte host that would result in changes of the  $\text{Li}^+$  transport mechanism from diffusion, coupled to the polymer matrix, to the one transported by the plasticizer.

The other task that we are concentrating on is understanding and characterization of the structural and transport properties of the reversibly adsorbed electrolytes on the model electrode surfaces during battery operation. Four types of electrolytes in contact with the model electrode that is non-blocking for  $\text{Li}^+$  but blocking for anions are currently simulated. Specifically, we are performing MD simulations on liquid electrolyte EC/LiTFSI, ionic liquid  $\text{LiTFSI}-(\text{EO})_{30}-\text{LiTFSI}$ , gel electrolyte consisting of (trifluoromethanesulfonyl) imide anion immobilized on the comb-branched polymer-host side chain plasticized with EC, and polymer electrolyte based on PTMO/LiTFSI. Electrolyte is subjected to the electric field resulting in development of concentration profiles that are currently analyzed as a function of distance from the model electrode surface. Parameters of ion and solvent interactions with the model electrode surface were adjusted in order to provide a significant number of Li intercalation events on the time scale of simulations. After steady state is reached, we plan to perform analysis of the structure and dynamics in the Helmholtz plane and diffuse double layer developed next to the model electrode surface.

The many-body polarizable force field has been developed for dilithium alkyl carbonate – a commonly observed component of the outer SEI layer. Transport and structural properties of dilithium alkyl carbonate are currently studied as a function of temperature.

**Reasons for Changes from Original Milestones:** N/A



## BATT TASK 4 CATHODES

### TASK STATUS REPORT

**PI, INSTITUTION:** M. Thackeray, Argonne National Laboratory

**TASK TITLE:** Cathodes - Novel Materials

**SYSTEMS:** High-voltage, high energy: Gr/LiPF<sub>6</sub>+EC:DEC/LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>  
High-voltage, high power: Gr/LiBOB+γBL:EA/LiMn<sub>2</sub>O<sub>4</sub>

**BARRIER:** Cost and abuse tolerance of Li-ion batteries

**OBJECTIVE:** To develop low cost, high-energy and high-power Mn-oxide-based cathodes.

**APPROACH:** Our approach is to search for, characterize, and develop low-cost manganese oxide cathodes for Li-ion cells. We will continue to focus our work on high-voltage, high-capacity layered lithium-manganese oxide ‘composite’  $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$  structures with particular emphasis on electrodes in which  $\text{M}' = \text{Mn}$  and  $\text{M} = \text{Mn, Ni, Co}$  that operate between 3.0 and 4.8 V *vs.* Li<sup>0</sup>. These materials are showing excellent promise to replace LiCoO<sub>2</sub> as the cathode of choice for Li-ion batteries; they also hold promise for high-power applications. We will also attempt to exploit high-potential LiM<sub>2</sub>O<sub>4</sub> spinel materials (4.0-5.0 V *vs.* Li<sup>0</sup>) for high-power batteries. In conjunction with our anode project (Task 2.1), we will explore the electrochemical properties and the abuse tolerance of high-potential layered and spinel cathodes against graphite and low-potential metal oxide anodes.

**STATUS OCT. 1, 2004:** It was demonstrated that a rechargeable capacity of 170-180 mAh/g could be delivered by  $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  composite electrodes in Li cells for 100 cycles between 4.5 and 3.0 V at 50°C. It was discovered that the irreversible capacity loss on the initial cycle could be reduced by pre-conditioning the electrodes with acid. A capacity in excess of 110 mAh/g was achieved from spinel electrodes when cycled between 5.0 and 3.5 V *vs.* Li which augers well for the development of stable high-voltage (>4.5 V) Li-ion cells. Evaluation of high-potential layered and spinel cathodes against metal oxide anodes had been initiated.

**EXPECTED STATUS SEPT. 30, 2005:** Improvements in the electrochemical performance of  $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$  electrodes will have been achieved. High-capacity  $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$  layered electrodes and high-rate LiM<sub>2</sub>O<sub>4</sub> (4.0 – 5.0 V) spinel electrodes with a high Mn content will have been evaluated against graphite and metal oxide negative electrodes.

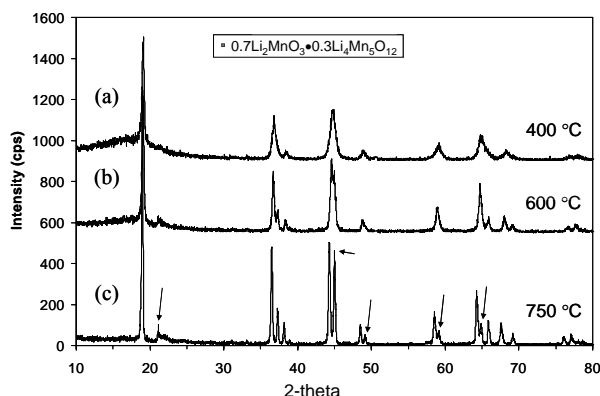
**RELEVANT USABC GOALS:** 300,000 shallow discharge cycles (HEV requirement); 10 year life, <20% fade over a 10-year period.

**MILESTONES (by 30 September 2005):** 1) Evaluate  $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$  composite electrodes with a high Mn content against a technical target of 200 mAh/g for 100 cycles between 4.8 and 3.0 V *vs.* Li<sup>0</sup> at room temperature and at 50°C; 2) Evaluate the rate capability and low-temperature behavior of layered  $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$  and spinel LiM<sub>2</sub>O<sub>4</sub> electrodes; and 3) evaluate the layered and spinel cathodes against graphite and metal oxide anodes.

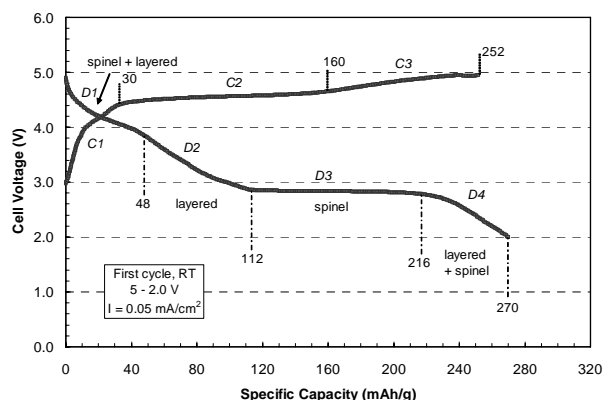
## PROGRESS TOWARD MILESTONES

We are extending our strategy of designing high-capacity ( $>200$  mAh/g) ‘composite’ electrode structures with two layered components (denoted  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ , in which M is predominantly Mn and Ni) to composite structures with layered and spinel components, (denoted  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiM}_2\text{O}_4$ ). Our ultimate goal is to design a bi-functional electrode structure with a high manganese content in which the layered component ensures a high capacity while the spinel component ensures high rate capability. The structural compatibility that exists between the (001) close-packed planes of layered  $\text{Li}_2\text{MnO}_3$  with the (111) planes of spinel  $\text{LiM}_2\text{O}_4$  compounds should, in principle, make the structural integration of the two components possible. For our initial investigations, we selected the lithium-manganese-oxide system  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{Li}_{1+y}\text{Mn}_{2-y}\text{O}_4$ .

Layered-spinel composite electrode structures were synthesized by reacting the required amounts of Li and Mn salts at various temperatures. The X-ray diffraction patterns of  $0.7\text{Li}_2\text{MnO}_3 \cdot 0.3\text{Li}_4\text{Mn}_5\text{O}_{12}$  products synthesized between 400 and 750 °C are shown in Fig. 1(a-c). Although the layered and spinel components have remarkably similar X-ray patterns, the layered component can be distinguished from the spinel component by peaks unique to the layered component, which are more readily observable in the product synthesized at 750 °C (arrowed in Fig. 1c). Heating the product from 400 to 750 °C releases oxygen, which drives the composition of the spinel component from  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  toward  $\text{LiMn}_2\text{O}_4$  (as monitored by an increase of the lattice parameter) and, at the same time, increases the concentration of the  $\text{Li}_2\text{MnO}_3$  component to maintain the required Li:Mn ratio in the structure.



**Figure 1.** XRD patterns of  $0.7\text{Li}_2\text{MnO}_3 \cdot 0.3\text{Li}_4\text{Mn}_5\text{O}_{12}$  products synthesized at various temperatures.



**Figure 2.** Initial charge/discharge profiles of a  $\text{Li}/0.7\text{Li}_2\text{MnO}_3 \cdot 0.3\text{Li}_4\text{Mn}_5\text{O}_{12}$  cell.

The initial charge and discharge profiles of a  $\text{Li}/0.7\text{Li}_2\text{MnO}_3 \cdot 0.3\text{Li}_4\text{Mn}_5\text{O}_{12}$  cell are shown in Fig. 2. The capacity delivered between 3 and 4.3 V during the initial charge to 5.0 V corresponds to the oxidation of a small amount of  $\text{Mn}^{3+}$  in the parent electrode. Thereafter, two voltage plateaus distinguish the removal of  $\text{Li}_2\text{O}$  from the layered and spinel components. The first plateau between 4.5 and 4.7 V is attributed predominantly to the extraction of  $\text{Li}_2\text{O}$  from the  $\text{Li}_2\text{MnO}_3$  component because this potential is consistent with removal of  $\text{Li}_2\text{O}$  from the  $\text{Li}_2\text{MnO}_3$  component of  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$  electrodes; the process at higher potential (4.7-5.0 V) is consistent with reports from Manthiram’s group of Li extraction from  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  at ~5 V. The discharge profile is consistent with a composite electrode having both spinel and layered-type structural features. Our preliminary data indicate that high rechargeable capacities ( $>200$  mAh/g) are achievable from these composite structures, consistent with our goals.

## TASK STATUS REPORT

**PI, INSTITUTION:** M.S. Whittingham, SUNY at Binghamton

**TASK TITLE - PROJECT:** Cathodes – Novel Materials

**SYSTEMS:** Li-Ion high voltage, high energy, and low-voltage/high stability

**BARRIER:** Lower-cost, higher-power, higher-capacity and abuse-tolerant safer cathodes

**OBJECTIVES:** The primary objectives are to find (a) lower-cost and higher-capacity cathodes, exceeding 200 Ah/kg, and (b) high-rate HEV compatible cathodes, both of which are based on environmentally benign materials.

**APPROACH:** Our cathode approach is to place emphasis on manganese dioxides, both pure and modified with other transition metals, using predominantly low-temperature synthesis approaches. These materials will be synthesized, and characterized both structurally and for thermal and chemical stability. All will be evaluated electrochemically in a variety of cell configurations.

**STATUS OCT. 1, 2004:** We have determined that layered manganese dioxides can be structurally stabilized, and that their electronic conductivity and cycling can be significantly enhanced by the addition of other transition metals. Addition of other transition metals also prevents structure change at low Li content to one-block or spinel structures, and changes oxygen evolution behavior. We have completed an evaluation of  $\text{LiFePO}_4$  as a base-case low-cost cathode, and shown that it is intolerant of deep over-discharge. We also have shown that vanadium oxides can be stabilized by the addition of ammonium and manganese ions to attain capacities above 200Ah/kg.

- $\text{LiFePO}_4$ : > 120 Ah/kg for 100 cycles at 1 mA/cm<sup>2</sup>.
- Layered  $\text{Li}_x\text{Co}_z\text{Ni}_y\text{Mn}_{1-y-z}\text{O}_2$ : 175 Ah/kg and 150 Ah/kg for 30 cycles at 1 and 2 mA/cm<sup>2</sup> respectively.
- Layered  $\text{A}_z\text{Mn}_{0.1}\text{V}_2\text{O}_5$  (A=  $\text{NH}_4$  or TMA):  $\geq 200$  Ah/kg for 6 cycles.

**EXPECTED STATUS SEPT. 30, 2005:** For low-cost Li-Ion cells, we expect to identify the changes in (a) electrochemistry, (b) oxygen evolution (abuse tolerance), (c) high rate capability (HEV), (d) coating effectiveness, and (e) the electronic conductivity of  $\text{LiMnO}_2$  structures as a function of substitution level as in  $\text{Li}_x\text{Mn}_{1-y-z}\text{Ni}_y\text{Co}_z\text{O}_2$ , so as to determine the optimum minimum substitution level. We will also have evaluated possible variants on iron phosphate as base-case cathodes, and explored some higher-capacity next-generation cathodes.

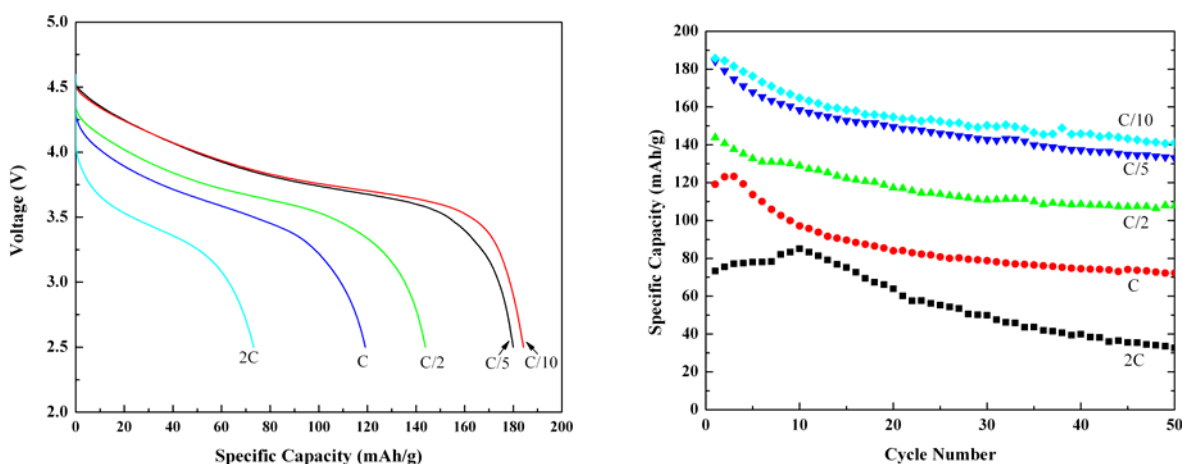
**RELEVANT USABC GOALS:** 300,000 shallow discharge cycles, and abuse tolerance to cell overcharge and short circuit

**MILESTONES:** Our major milestones this year are: (a) to characterize the electronically stabilized manganese oxide, determine the optimum substitution of Mn to obtain a stable high-rate abuse-tolerant cathode (including application to HEV), and to compare the best samples with iron phosphates by July 2005, and (b) to search for, identify and characterize some new low-cost higher energy density cathode materials and to compare the best samples with the base-line chemistries (continuing).

## PROGRESS TOWARD MILESTONES

**Iron Phosphates.** This quarter we continued our studies of lithium iron phosphate and related structures. Specifically we have been exploring the low-temperature hydrothermal synthesis again as a low-cost route to this material. We have successfully synthesized this material from 120–200°C with the same lattice parameters as the high-temperature material and with minimal iron on the Li site. In the next quarter we will be investigating the electrochemistry of this material.

**Layered Oxides.** Major effort this quarter continued on the characterization and evaluation of the mixed metal oxides,  $\text{Li}_x\text{Mn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$ . This has been a joint effort with Won-Sub Yoon of Brookhaven National Laboratory on the *in-situ* delithiation, and with colleagues at NIST on neutron diffraction studies of the nickel ordering. The data are presently being analyzed, and the first indications are that any phase transitions are smeared out, which might be expected to enhance the cycle capacity of this material. This same compound has been cycled over a range of cycling rates (same rate on charge and discharge, no topping-up on charge). The capacity is shown as a function of rate in Fig.1 below, and it can be seen that at low rates the capacity is about 180 mAh/g. The capacity of these cells, cycled using a  $\text{LiPF}_6$  salt electrolyte, decays slightly upon cycling as also shown in Fig.1. Although the initial capacities were increased by using a higher charging cut-off voltage, there was only a minimal effect on the capacity after the first 20 cycles; after 50 deep cycles the capacity at a C/10 rate was 140 mAh/g for cut-off voltages of 4.4, 4.6, and 4.7 volts.



**Figure 1.** (left) Discharge curves of  $\text{Li}^+$  in  $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ , as a function of discharge rate and (right) the capacity of the same cells over the first 50 cycles.

**Further plans to meet or exceed milestones:** None

**Reason for changes from original milestones:** No changes

Publications and Presentations resulting from the work.

1. Y. Song, P.Y. Zavalij, M.S. Whittingham, " $\epsilon$ -VOPO<sub>4</sub>: Electrochemical Synthesis and Enhanced Cathode Behavior," *J. Electrochem. Soc.*, **152**, A721-A728 (2005).
2. M.S. Whittingham, "Advanced Batteries," March 29, 2005, Whitney Symposium, General Electric, Global Research, Niskayuna, NY.
3. Y. Song, P.Y. Zavalij, N.A. Chernova, and M.S. Whittingham, "Synthesis, Crystal Structure, Electrochemical and Magnetic Study of New Iron (III) Hydroxyl-Phosphates, Isostructural with Lipscombite," *Chem. Mater.*, **17**, 1139-1147 (2005).
4. M. Ma, N.A. Chernova, P.Y. Zavalij, and M.S. Whittingham, "Structural and Electrochemical Properties of  $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$ ," *Mater. Res. Soc. Proc.*, **835**, K11.3 (2005).
5. M.S. Whittingham, Y. Song, S. Lutta, P.Y. Zavalij, and N.A. Chernova, "Some Transition Metal (Oxy)Phosphates and Vanadium Oxides for Lithium Batteries," *J. Mater. Chem.*, **15** (2005). Feature Article available on-line.

## TASK STATUS REPORT

**PI, INSTITUTION:** M. Doeff, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Cathodes - Synthesis and Characterization of Cathode Materials for Rechargeable Lithium and Lithium-Ion Batteries

**SYSTEMS:** Low-voltage, high-stability ( $\text{LiFePO}_4$ ); high-voltage, high-energy ( $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ , new manganese oxides); and high voltage, high-power (new manganese oxides)

**BARRIERS:** Cost, cycle life, safety, energy density, and power density

**OBJECTIVES:** To develop low-cost cathodes based on benign materials (manganese oxides, lithium iron phosphates, etc.) having electrochemical characteristics (*e.g.*, cycle life, energy and power densities) consistent with the goals of the USABC and/or FreedomCar.

**APPROACH:** Cathode materials are synthesized by various means. Physical and electrochemical properties (*e.g.*, structure, surface characteristics) are measured in conjunction with members of the diagnostic tasks. Emphasis is placed on low-cost, structurally stable materials such as manganese oxides and lithium iron phosphate, as well as novel materials with the potential for high energy density.

**STATUS OCT. 1, 2004:** Electrochemical characterization of  $\text{Li}_x\text{Al}_y\text{Mn}_{1-y}\text{O}_{2+z}$  O2/O3 intergrowths was completed. Experiments determining the optimum amount of pyromellitic acid (PA) for carbon-coating  $\text{LiFePO}_4$  were completed, and those using Fe promoters of graphene formation are underway.

**EXPECTED STATUS SEPT. 30, 2005:** Initial screening of novel manganese oxides for abuse-tolerance will be complete, and materials will be recommended for high-power applications based on results. *In situ* carbon structure, electrochemical performance, and synthetic parameters (*e.g.*, promoter-to-PA ratios) used in making coated  $\text{LiFePO}_4$  will be correlated. New manganese oxide structures without Ni or Co substituents for high-energy-density applications will continue to be surveyed.

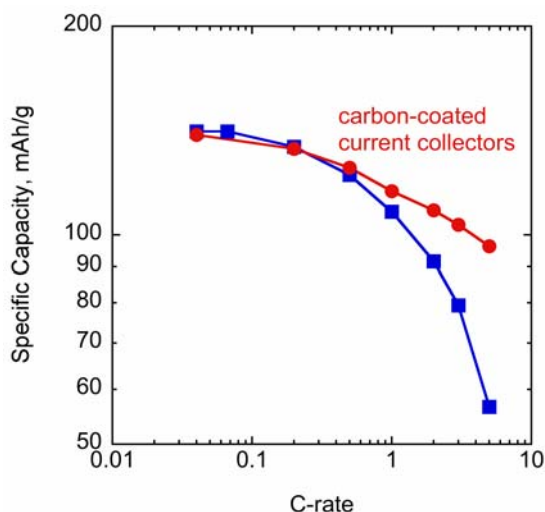
**RELEVANT USABC GOALS:** 10-year life, < 20% capacity fade over a 10-year period.

### MILESTONES:

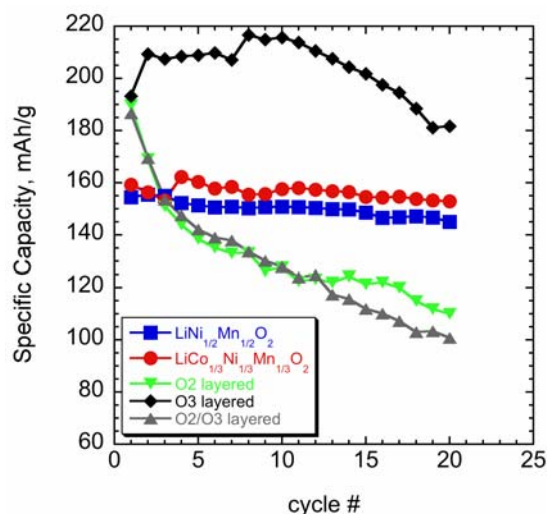
- a) Determine best synthetic conditions (promoter-to-PA ratios, etc.) for carbon-coating  $\text{LiFePO}_4$ . (June 2005)
- b) Recommend the most abuse-tolerant manganese oxide structures for potential HEV applications, and highest energy density manganese oxides containing no Ni or Co for potential high-energy applications. (Sept. 2005)

## PROGRESS TOWARD MILESTONE (a)

**4.3a.** The rate capability of the best-performing  $\text{LiFePO}_4$  from this laboratory is substantially improved when carbon-coated current collectors are used (Fig. 1). Mathematical modeling (V. Srinivasan) indicates that this material nearly matches the performance at high rates of  $\text{LiFePO}_4$  samples from Phostech, but is worse at low rates. This is most likely attributable to a wide particle size distribution. Future work will be devoted towards decreasing this and should result in further improvement. Several samples processed with ferrocenecarboxylic acid and pyromellitic acid are also currently under test.



**Figure 1.** Rate data for  $\text{Li}/\text{LiFePO}_4$  cells containing cathode materials prepared with 6% PA and 1% ferrocene promoters (carbon content 1.45 wt%).



**Figure 2.** Capacity at  $55^\circ\text{C}$  as a function of cycle number for  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ ,  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  and layered manganese oxides.

**4.3b.** Samples of  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ ,  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ , layered, and spinel manganese oxides were stored in a  $1\text{M LiPF}_6$  1:2 EC/DMC solution at  $55^\circ\text{C}$  for several weeks, and test strips were used to determine if metal dissolution was occurring as a function of time. Li cells containing these materials were cycled at the same temperature (Fig. 2). Results indicate that spinel and O3 layered materials underwent the most Mn dissolution.  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  and  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  cycle well at elevated temperature, while O2 and O2/O3 layered manganese oxides show rapid fading. Somewhat surprisingly, the O3 compound shows higher capacity at elevated temperatures than at room temperature, but fading still occurs. This work will be extended to tunnel manganese oxides in the following quarter.

**Further plans to meet or exceed milestones** N/A

**Reason for changes from original milestones** N/A

### Publications and Presentations:

- 1) "Layered Manganese Oxide Intergrowth Electrodes for Rechargeable Lithium Batteries: Part 1. Substitution with Co or Ni", Mickaël Dollé, Sébastien Patoux and Marca M. Doeff, *Chem. Mater.*, **17**, 1036 (2005).
- 2) "Layered Manganese Oxide Intergrowth Electrodes for Rechargeable Lithium Batteries: Part 2. Substitution with Al", Sébastien Patoux, Mickaël Dollé, and Marca M. Doeff, *Chem. Mater.*, **17**, 1044 (2005).

## TASK STATUS REPORT

**PI, INSTITUTION:** J.B. Goodenough, University of Texas at Austin

**TASK TITLE - PROJECT:** Cathodes - Novel Materials

**SYSTEMS:** Li secondary battery

**BARRIERS:** Cost, cycle life, safety, and energy density

**OBJECTIVES:** To evaluate alternative *cathode* materials for a lithium-ion battery.

**APPROACH:** The universal motif of cathodes in rocking chair  $\text{Li}^+$ -ion batteries is one of immobilized redox centers that are accessible to electrons from the current collector and  $\text{Li}^+$  ions from the electrolyte. Immobilization ensures that the redox units do not transfer to and subsequently poison the anode. Our research is centered around high-power cathodes for the purpose of EV and HEV's. This translates into pure or composite materials which allow for transfer of electrons *and*  $\text{Li}^+$  ion with little or no resistance. We are currently pursuing three different avenues of research: (1) new materials based on conventional oxide structures with proven high rate capabilities, (2) new cathode schemes based on conductive polymers which may serve either as self-contained cathodes or as a new conductive binder in more conventional composite cathodes, and (3) substitution into the environmentally benign and cost-effective  $\text{LiFePO}_4$  to improve rate capabilities.

**STATUS OCT. 1, 2004:** Well-ordered  $\text{LiNi}_{1-x}\text{Mn}_x\text{O}_2$  has been prepared and battery testing has shown good cyclability. A principle for predicting cation order/disorder in layered materials with an  $\alpha\text{-NaFeO}_2$  structure has been developed. Preliminary rate tests are in progress.

### EXPECTED STATUS SEPT. 30, 2005:

- Electrochemical testing of our high-rate layered material to elucidate the limiting parameter will have been completed.
- Preliminary analysis of substitution into the Fe site of  $\text{LiFePO}_4$  will have been completed.
- The feasibility of polypyrrole as a conducting binder/scaffolding will have been explored.

**RELEVANT USABC GOALS:** 10-year life, < 20% capacity fade over a 10-year period.

### MILESTONES:

1. Electrochemical testing of our high-rate layered material to elucidate the limiting parameter. (Feb. 2005)
2. Preliminary analysis of substitution into the Fe site of  $\text{LiFePO}_4$ . (Aug. 2005)

## PROGRESS TOWARD MILESTONES

In our previous quarter, we had succeeded to attach chemically ferrocene groups to every other pyrrole of a polypyrrole (PPy) backbone, and Fig. 1 compares its discharge/charge curves vs.  $\text{Li}^+/\text{Li}^0$  with that of PPy without a redox-couple attachment. A plateau near 3.5 V is clearly associated with the ferrocene redox couple, but the capacity remains too small. Therefore, we extended the concept to physically attach  $\text{LiFePO}_4$  to PPy. Figure 2 compares discharge/charge curves vs.  $\text{Li}^+/\text{Li}^0$  of a  $\text{LiFePO}_4$ /PPy composite containing no carbon black or PTFE with those of the conventional  $\text{LiFePO}_4$ /C/PTFE composite in a weight ratio 75:20:5. At a C/5 rate, the capacity is increased from the 105 mAh/g of the conventional composite to 132 mAh/g of the composite with PPy.

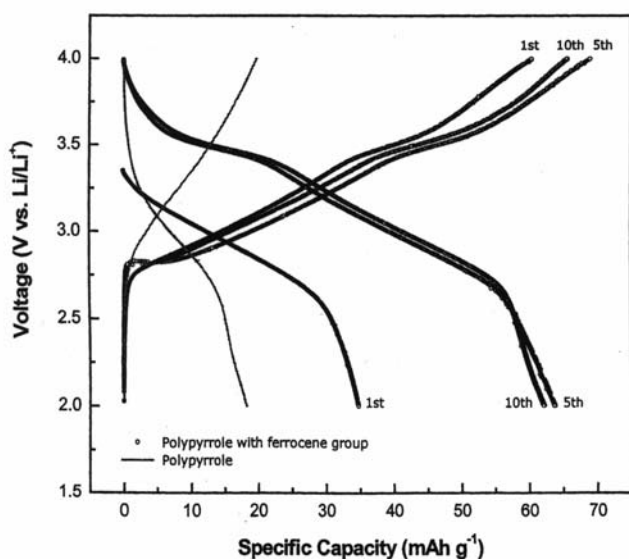


Figure 1. PPy with ferrocene group.

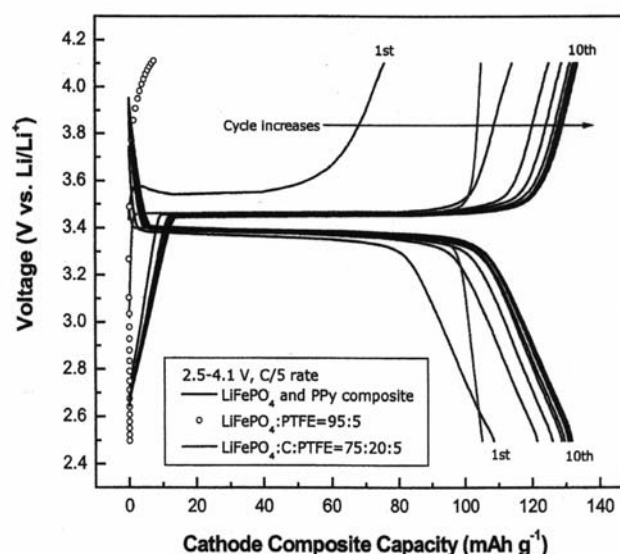


Figure 2. Cathode composite capacities.



## TASK STATUS REPORT

**PI, INSTITUTION:** A. Manthiram, University of Texas at Austin

**TASK TITLE - PROJECT:** Cathodes - Superior Capacity Retention, High-Rate Spinel Manganese Oxide Compositions

**SYSTEMS:** Spinel manganese oxides

**BARRIERS:** Cycle life, elevated-temperature storage, power density, and energy density

**OBJECTIVES:** To develop low-cost spinel manganese oxide compositions that can offer excellent capacity retention, high rate, low irreversible capacity loss, and good storage characteristics at elevated temperatures.

**APPROACH:** Our approach is to develop a firm scientific understanding of the factors that control/influence the electrochemical performance of the spinel oxide cathodes and utilize the knowledge gained to design and develop high performance spinel manganese oxide compositions. In this regard, a variety of single and multiple cationic substitutions as well as an optimization of the microstructure and morphology are being pursued.

**STATUS OCT. 1, 2004:** A variety of multiple cationic substitutions in the spinel  $\text{LiMn}_2\text{O}_4$  system and an evaluation of the electrochemical performances of the various compositions have established a clear correlation of the electrochemical properties to some basic materials parameters such as the initial manganese valence and the lattice parameter difference  $\Delta a$  between the two cubic phases formed during the charge-charge process.

**EXPECTED STATUS SEPT. 30, 2005:** Evaluation of the optimized  $\text{LiMn}_{2-y-z}\text{Ni}_y\text{Li}_z\text{O}_4$  and  $\text{LiMn}_{2-y-z-\eta}\text{M}_y\text{Li}_z\text{M}'_\eta\text{O}_4$  (M and M' = transition and non-transition metal ions) spinel oxide compositions (4 V) in Li-ion cells, identification of the factors that control the electrochemical performances of the cation-substituted 5 V spinel oxide system  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ , and a comparison of the factors with those of the 4 V spinel oxide cathodes.

**RELEVANT USABC GOALS:** 10-year life, < 20 % capacity fade over a 10-year period

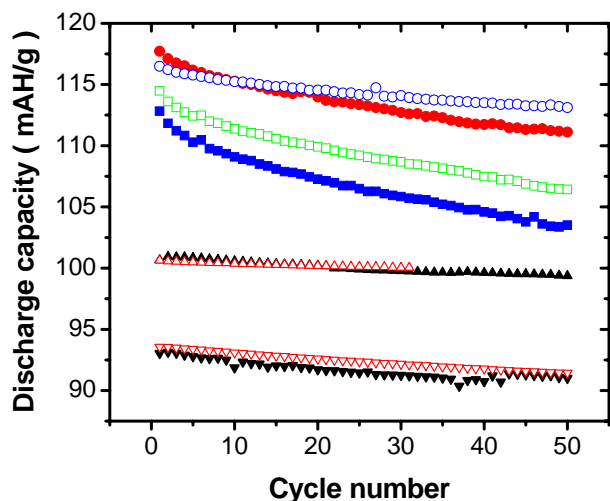
### MILESTONES:

1. Evaluation of the optimized 4 V spinel oxide cathodes in Li-ion cells. (Mar. 2005)
2. Identification of the factors controlling the electrochemical performances of the cation-substituted 5 V spinel oxide system  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ . (Sept. 2005)

## PROGRESS TOWARD MILESTONES

In continuation of our multiple cationic substitutions for Mn in the 4 V spinel oxide cathodes, we have now evaluated the storage performances of  $\text{LiMn}_{1.85}\text{Al}_{0.075}\text{Li}_{0.075}\text{O}_4$  and  $\text{LiMn}_{1.85}\text{Ni}_{0.04}\text{Al}_{0.035}\text{Li}_{0.075}\text{O}_4$  and compared the data with those of our previous best compositions such as  $\text{LiMn}_{1.85}\text{Li}_{0.075}\text{Ni}_{0.075}\text{O}_4$ . The triply substituted  $\text{LiMn}_{1.85}\text{Ni}_{0.04}\text{Al}_{0.035}\text{Li}_{0.075}\text{O}_4$  composition is found to show slightly better storage characteristics and elevated temperature cyclability than the doubly substituted  $\text{LiMn}_{1.85}\text{Li}_{0.075}\text{Ni}_{0.075}\text{O}_4$  and  $\text{LiMn}_{1.85}\text{Al}_{0.075}\text{Li}_{0.075}\text{O}_4$  compositions. Although the doubly and triply substituted spinel oxide compositions show superior cyclability, rate capability, and storage characteristics with low irreversible capacity loss compared to the unsubstituted  $\text{LiMn}_2\text{O}_4$  cathode, they generally exhibit lower capacities than  $\text{LiMn}_2\text{O}_4$ . With an aim to increase the capacity values while still preserving the other improved electrochemical performance parameters, we have pursued the substitution of small amounts of fluorine for oxygen in the anionic lattice along with the cationic substitutions to obtain compositions such as  $\text{LiMn}_{1.9}\text{Ni}_{0.1}\text{O}_{4-z}\text{F}_z$ ,  $\text{LiMn}_{1.9}\text{Ni}_{0.05}\text{Li}_{0.05}\text{O}_{4-z}\text{F}_z$ , and  $\text{LiMn}_{1.85}\text{Ni}_{0.075}\text{Li}_{0.075}\text{O}_{4-z}\text{F}_z$  with  $0 \leq z \leq 0.2$ . The fluorine substituted oxyfluoride spinel compositions synthesized by conventional solid-state methods exhibit 5-10 mAh/g higher capacities than the corresponding oxide counterparts as seen in Fig. 1 due to a lowering of the manganese valence. Also, the fluorine substitution leads to a further improvement in cyclability both at room temperature and at 60°C while maintaining similar rate capabilities. For example,  $\text{LiMn}_{1.85}\text{Ni}_{0.075}\text{Li}_{0.075}\text{O}_{3.8}\text{F}_{0.2}$  exhibits an excellent capacity retention with 1% fade in 50 cycles compared to 2% fade for  $\text{LiMn}_{1.85}\text{Ni}_{0.075}\text{Li}_{0.075}\text{O}_4$ . We have also evaluated the manganese dissolution by soaking the spinel oxide powders in 1 M  $\text{LiPF}_6$  in ethylene carbonate/diethyl carbonate electrolyte at 55°C for 7 days. The fluorine-substituted compositions exhibit a lower amount of manganese dissolution (1.5–2.0%) than the corresponding oxide compositions (2.5–3.0%) possibly due to stronger metal-fluorine bonds.

Additionally, we have compared the  $\text{LiMn}_2\text{O}_4$  and  $\text{LiMn}_{1.88}\text{Ni}_{0.06}\text{Li}_{0.06}\text{O}_4$  cathodes at various stages of cycling by micro-Raman spectroscopy in collaboration with the University of Puerto Rico at San Juan. While the  $\text{LiMn}_2\text{O}_4$  cathode shows in the fully discharged state after 5 cycles the presence of >35% of the second cubic phase ( $F\bar{4}3m$ ) formed during the charge-discharge cycling, the cation-substituted  $\text{LiMn}_{1.88}\text{Ni}_{0.06}\text{Li}_{0.06}\text{O}_4$  cathode retains predominantly the original  $Fd\bar{3}m$  cubic phase with <20% of the second cubic phase ( $F\bar{4}3m$ ) in the fully discharged state after 50 cycles, attesting to its better cyclability compared to  $\text{LiMn}_2\text{O}_4$ .



**Figure 1.** Electrochemical cycling performances of spinel oxide and oxyfluoride cathodes at 25 and 60°C at C/5 rate:

- :  $\text{LiMn}_{1.9}\text{Ni}_{0.1}\text{O}_4$  (25°C)
- :  $\text{LiMn}_{1.9}\text{Ni}_{0.1}\text{O}_{3.9}\text{F}_{0.1}$  (25°C)
- :  $\text{LiMn}_{1.9}\text{Ni}_{0.1}\text{O}_{3.8}\text{F}_{0.2}$  (25°C)
- :  $\text{LiMn}_{1.9}\text{Ni}_{0.05}\text{Li}_{0.05}\text{O}_{3.8}\text{F}_{0.2}$  (25°C)
- ▽:  $\text{LiMn}_{1.85}\text{Ni}_{0.075}\text{Li}_{0.075}\text{O}_4$  (25°C)
- ▲:  $\text{LiMn}_{1.85}\text{Ni}_{0.075}\text{Li}_{0.075}\text{O}_{3.8}\text{F}_{0.2}$  (25°C)
- ▼:  $\text{LiMn}_{1.85}\text{Ni}_{0.075}\text{Li}_{0.075}\text{O}_4$  (60°C)
- △:  $\text{LiMn}_{1.85}\text{Ni}_{0.075}\text{Li}_{0.075}\text{O}_{3.8}\text{F}_{0.2}$  (60°C)

## BATT TASK 5 DIAGNOSTICS

### TASK STATUS REPORT

**PI, INSTITUTION:** R. Kostecki, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Diagnostics - Electrode Surface Layers

**SYSTEMS:** High-voltage, high-energy: Gr/LiPF<sub>6</sub>+EC:DEC/LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>,  
Low-voltage, high-stability: Gr/LiPF<sub>6</sub>+EC:DEC/LiFePO<sub>4</sub>,  
High-voltage, high-power: Gr/LiBOB+γBL:EA:LiMn<sub>2</sub>O<sub>4</sub>

**BARRIER:** Short lithium battery calendar/cycle lifetimes.

**OBJECTIVES:** The primary objective is to establish direct correlations between electrode surface chemistry, interfacial phenomena, and cell power or capacity decline.

**APPROACH:** Our approach is to use *in-situ* and *ex-situ* Raman microscopy, scanning probe microscopy (SPM), spectroscopic ellipsometry, scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and standard electrochemical methods to characterize cell components taken from baseline BATT Program cells, fresh electrode materials, and thin-film or single-particle model electrodes. Data to be collected include changes in electrode surface morphology, structure, electronic conductivity, electrode surface chemistry, and SEI thickness and composition, all of which accompany cell cycle-life tests.

**STATUS OCT. 1, 2004:** We expect to develop better understanding of the mechanism of carbon retreat in the composite LiAl<sub>0.05</sub>Ni<sub>0.8</sub>Co<sub>0.15</sub>O<sub>2</sub> cathodes and its impact on the cathode electrochemical performance upon cycling and storage in LiPF<sub>6</sub>-EC-EMC electrolyte at elevated temperatures. We intend to identify and characterize physico-chemical processes, which are responsible for this effect, and establish possible links with other detrimental phenomena. The correlations between electrode history, electrode surface properties, and temperature for baseline LiAl<sub>0.05</sub>Ni<sub>0.8</sub>Co<sub>0.15</sub>O<sub>2</sub> cathodes will be developed. We expect to determine and verify the key elements for high-rate performance of LiFePO<sub>4</sub> composite cathodes, *i.e.*, the effect of residual carbon and solid-solution doping by metals supervalent to Li<sup>+</sup>.

**EXPECTED STATUS SEPT. 30, 2005:** We expect to define relationships between electrochemical performance and limitations of BATT baseline systems and cell history, abuse tolerance, electrodes surface properties, and interfacial phenomena. We intend to develop good understanding of the key elements for good electrochemical performance of LiFePO<sub>4</sub>, LiMn<sub>2</sub>O<sub>4</sub>, and LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> composite cathodes. We anticipate determining the mechanism of graphite disordering in composite anodes and carbon retreat in composite cathodes, and evaluate their impacts on long-term Li-ion cell performance. We also expect to develop an experimental methodology to carry out exploratory *in-situ* spectroscopy and microscopy studies of single-particle electrodes to characterize BATT baseline electrode materials.

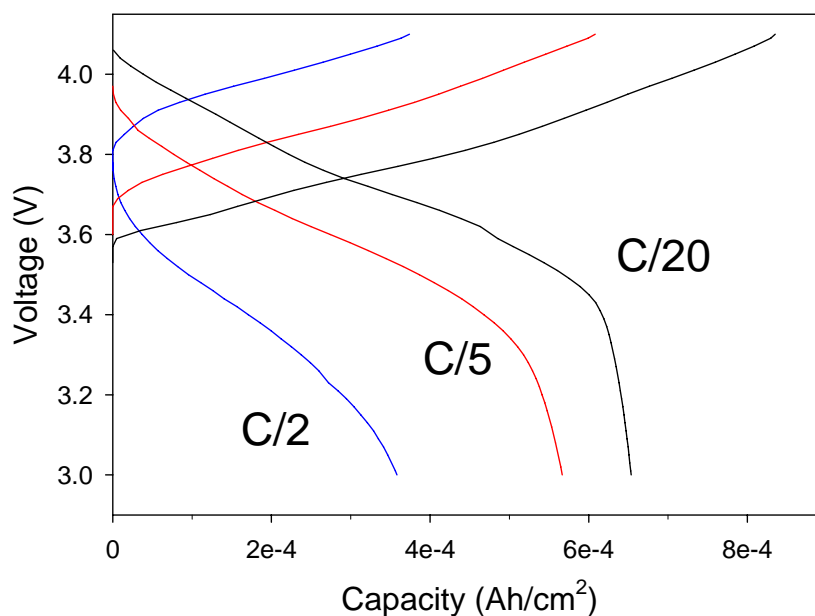
**RELEVANT USABC GOALS:** 15 year life, 30 ohm-cm<sup>2</sup> area-specific impedance, 300,000 shallow discharge cycles.

**MILESTONES:** (a) Quantitative and qualitative analysis of carbon retreat from composite cathodes by <sup>13</sup>C distribution examination in model Li-ion cells by March 2005. (b) Preliminary evaluation of *in-situ* microwave-assisted synthesis of graphitic carbon matrix for composite cathodes by June 2005.

## PROGRESS TOWARD MILESTONES

Our primary objective in the second quarter of FY05 was to carry out in-depth diagnostic studies of the mechanism of carbon retreat in composite cathodes and determine its impact on cathode and anode electrochemical performance upon cycling and storage in LiPF<sub>6</sub>-EC-EMC electrolyte at elevated temperatures. The observed carbon retreat was determined and verified in composite LiAl<sub>0.05</sub>Ni<sub>0.8</sub>Co<sub>0.15</sub>O<sub>2</sub>, LiFePO<sub>4</sub>, and LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> cathodes, and it was clearly linked with other detrimental phenomena that led to the observed cell degradation, *e.g.*, increased carbon disorder observed in graphite anodes.

To study in detail the movement of carbon additives in composite cathodes and its possible implications for battery performance, <sup>13</sup>C-enriched composite LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> cathodes were manufactured in collaboration with Vince Battaglia (Task 1.1). The new electrodes consist of 84% LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>, 4% <sup>12</sup>C graphite, 4% <sup>13</sup>C carbon black, and 4% PVDF binder. Surface chemical composition, morphology, and electronic conductivity of fresh composite electrodes were characterized by Raman microscopy, SEM, and current-sensing AFM. <sup>13</sup>C-enriched composite cathodes display physico-chemical properties very similar to what was observed for Gen-2 LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> cathodes with standard <sup>12</sup>C acetylene black additive. The electrochemical behavior of the <sup>13</sup>C-enriched cathode was tested in Swagelok cells *vs.* Li metal anode (Fig. 1). A dozen <sup>13</sup>C-enriched composite LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>/1.2 M LiPF<sub>6</sub> EC:EMC (3:7) /Li metal Swagelok cells, and <sup>13</sup>C-enriched composite LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>/1.2 M LiPF<sub>6</sub> EC:EMC (3:7)/MAG-10 graphite pouch cells were manufactured. Electrochemical calendar life/cycle life tests of these cells at room temperature and at 45°C are currently being carried out. Post-mortem diagnostic analysis of tested cells with <sup>13</sup>C-enriched cathodes will be conducted in the coming weeks. We expect to accomplish the milestone (a) ~2 months later that it was previously planned, *i.e.*, in July 2005. The delay is mainly caused by time-consuming processes of electrode manufacturing, cell assembly/optimization, and long life/cycle testing.



**Figure 1.** Charge-discharge curves for <sup>13</sup>C-enriched composite LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> cathode *vs.* Li metal in 1.2 M LiPF<sub>6</sub> EC:EMC (3:7) electrolyte.

## TASK STATUS REPORT

**PI, INSTITUTION:** W.-S. Yoon and X.-Q. Yang, Brookhaven National Laboratory

**TASK TITLE - PROJECT:** Diagnostics - Battery Materials: Structure and Characterization

**SYSTEMS:** High-power Li-ion, high-energy Li-ion

**BARRIER:** Short lithium battery lifetimes

**OBJECTIVES:** The primary objective is to determine the contributions of electrode material changes, interfacial phenomena, and electrolyte decomposition to cell capacity and power decline. The results of these studies will be used to guide exploratory research for new cathode, anode, and electrolyte materials for high-power Li batteries.

**APPROACH:** Our approach is to use a combination of *in situ*, *ex situ*, and time-resolved synchrotron techniques to characterize electrode materials and electrodes taken from baseline BATT Program cells. *Ex situ* soft X-ray absorption spectroscopy (XAS) will be used to distinguish between surface and bulk processes on electrodes using both electron yield (EY) and fluorescence yield (FY) detectors. Time-resolved X-ray diffraction technique will also be used to understand the reactions that occur in charged cathodes at elevated temperatures in the presence of electrolyte. Hard and soft XAS will be used to elucidate the charge-compensation mechanisms for cathode materials during electrochemical cycling. This work will be carried out in collaboration with other BATT members.

**STATUS OCT. 1, 2004:** In FY 2004 comparative studies between Gen2 ( $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ ) cathode and  $\text{LiMn}_2\text{O}_4$  spinel cathode have been completed using *in situ* X-ray diffraction (XRD) technique. Both cathodes were cycled at room temperature and 55°C. We have developed time-resolved XRD techniques using image plate detectors (IPD), and the thermal stability study of cathode materials at elevated temperatures in the presence of electrolyte is ongoing. We completed the *in situ* hard X-ray XAS and XRD work on  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  electrodes. Synchrotron based X-ray studies on the effect of new electrolytes and additives on the stability of  $\text{LiMn}_2\text{O}_4$  electrodes at elevated temperatures are ongoing.

**EXPECTED STATUS SEPT. 30, 2005:** We expect to complete the *ex situ* soft X-ray XAS work on  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  electrodes during the cycling process. We also expect to complete the *in situ* XRD work on  $\text{LiFePO}_4$  during electrochemical cycling at elevated temperatures. *In situ* XRD work on surface-coated  $\text{LiMn}_2\text{O}_4$  spinel cathode materials will be completed. Soft X-ray XAS using partial electron yield and fluorescence yield detectors will be applied to various cathode materials at the O, F, and P K edges and at the  $L_3$  and  $L_2$  edges of the 3d transition metals.

**RELEVANT USABC GOALS:** 15 year life, < 20% capacity fade over a 10-year period.

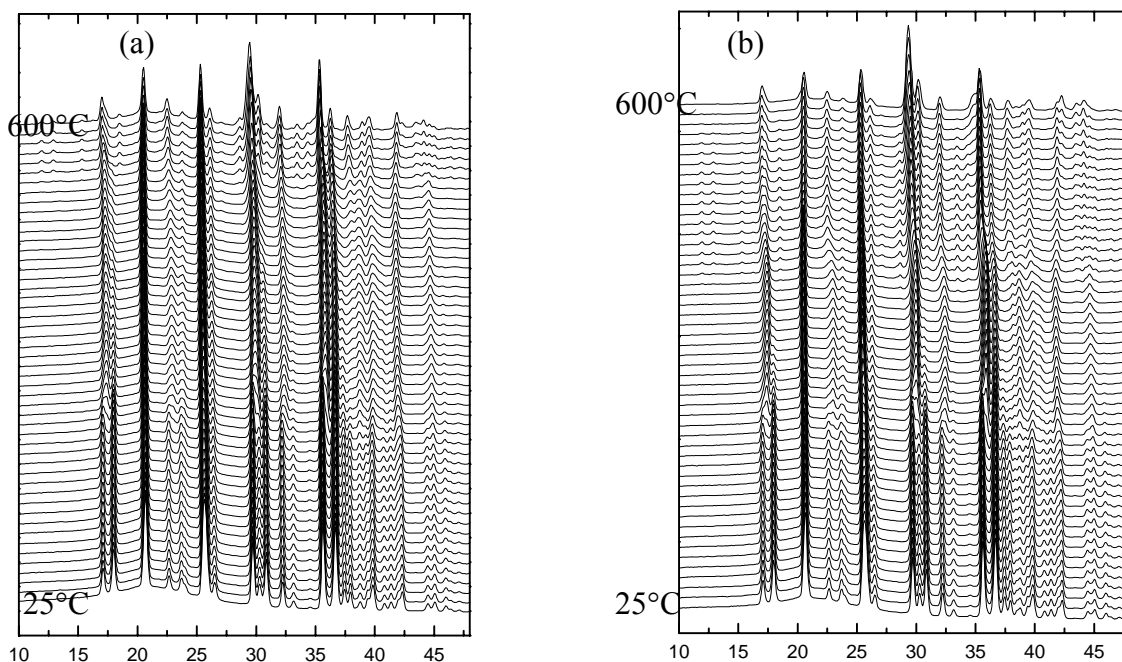
### MILESTONES:

- 1) Complete *ex situ* soft X-ray XAS on  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  during cycling. (Apr. 2005)
- 2) Complete *in situ* XRD work on surface-coated  $\text{LiMn}_2\text{O}_4$  spinel cathode materials. (Oct. 2005)

## PROGRESS TOWARD MILESTONES

We have used the *in situ* time-resolved XRD technique to monitor temperature-induced structural changes in carbon-coated  $\text{LiFePO}_4$  provided by Dr. Zaghib of Hydro-Québec. Studies were carried out on charged electrodes in the absence and presence of electrolyte. The electrolyte accelerates thermal decomposition of the charged cathode material. The presence of the electrolyte changes the paths of the structural changes and lowers the temperatures for onset of the reactions. As the extent of Li-ion deintercalation increases, the thermal decomposition takes place at a less-elevated temperature. Time-resolved XRD patterns for  $\text{Li}_{0.5}\text{FePO}_4$  in the absence and presence of electrolyte are seen in Fig. 1 (a) and (b), when heated from 25 to 600°C. The structure of the charged  $\text{Li}_{1-x}\text{FePO}_4$  cathode with electrolyte shows dramatic changes with increasing temperature compared to that of the charged  $\text{Li}_{1-x}\text{FePO}_4$  cathode without electrolyte. In the absence of electrolyte no structural decompositions are seen until ~515°C. In the presence of electrolyte, decomposition reactions can be seen as low as ~390°C. We observed a temperature-driven solid solution of  $\text{Li}_x\text{FePO}_4$  below decomposition temperatures of the charged  $\text{Li}_{1-x}\text{FePO}_4$  cathode with or without electrolyte as recently reported by Dr. Masquelier's group. The formation of the temperature-driven solid solution of  $\text{Li}_x\text{FePO}_4$  is much clearer in the cathode with electrolyte.

We continue to collaborate with other members of the BATT program (C. Grey, K. Zaghib, and S. Whittingham). Preliminary *in situ* XRD results of  $\text{Li}_{1-x}\text{Mn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$  from Whittingham's group indicate that the structural behavior of  $\text{Li}_{1-x}\text{Mn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$  during charge is quite different from that of  $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  cathodes. Compared with the structural changes of the  $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  cathode during charge, the phase transition boundaries in  $\text{Li}_{1-x}\text{Mn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$  cathode are smeared out. Other differences in the structural changes indicate the better structural stability of the  $\text{Li}_{1-x}\text{Mn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$  cathode.



**Figure 1.** Time-resolved XRD patterns for  $\text{Li}_{0.5}\text{FePO}_4$  in the absence (a) and presence (b) of electrolyte, when heated from 25 to 600°C.

## TASK STATUS REPORT

**PI, INSTITUTION:** P.N. Ross, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Diagnostics – Interfacial and Reactivity Studies

**SYSTEMS:** High-power battery

**BARRIER:** Short battery lifetime

**OBJECTIVES:** The primary objective is to establish direct correlations between electrode surface changes, interfacial phenomena, and cell failure.

**APPROACH:** Our approach is to use *in situ* Fourier transform infrared (FTIR) spectroscopy to study the *interfacial chemistry* in model electrode/electrolyte systems. The spectrometer optics and spectroelectrochemical cell have a special design that enables any electrode material to be studied. Model systems to be studied this year include new Mn-based cathode materials and new Sb-based anodes. The FTIR spectroscopy will be accompanied by classical electroanalytical methods such as cyclic voltammetry and the rotating ring-disk electrode (RRDE).

**STATUS OCT. 1, 2004:** The oxidation and reduction chemistry of the new Li-ion battery electrolyte salt LiBOB has been determined. The oxidative stability of GEN2 Li-ion battery electrolyte with the new Mn-based cathodes materials has been determined. The composition of the SEI layer on Sb-based anodes in PC-based electrolyte is under investigation.

**EXPECTED STATUS SEPT. 30, 2005:** The composition and stability of the SEI layer on Sb-based anodes in PC-based electrolyte will be known. The predicted advantages of a Sb-based anode *vs.* carbon/graphite anode for the high-power battery application will be established. Irreversible changes to the SEI layer of GEN2 anodes due to cycling at low temperature will be determined.

**RELEVANT USABC GOALS:** 15-year life, < 20% capacity fade over a 15-year period.

### MILESTONES:

- 1) Determine the potential advantages of a Sb-based anode *vs.* carbon/graphite anode for the high-power battery application based on differences in composition and stability of the SEI layer. (May 2005)
- 2) Determine the nature of irreversible changes to the SEI layer of GEN2 anodes due to cycling at low temperature. (Sept. 2005)

## PROGRESS TOWARDS MILESTONES

### Interfacial Chemistry at Low Temperature

We initiated the study of interfacial chemistry in Li-ion batteries at low temperatures. The first experiments have focused on interfacial phenomena observed with GEN2 anodes (MAG-10) in different electrolytes, standard GEN2 and a low-temperature version of GEN2 electrolyte, EC:PC:DMC (1:1:3) with 1 M LiPF<sub>6</sub>. Swagelok cells were used with Li counter electrodes, and *ex-situ* analysis of the graphite anodes was carried out using a combination of FTIR and XPS. Parallel experiments on Li deposition on non-carbon (Ni) electrodes were performed in the same electrolytes to establish the FTIR signatures of the SEI layer on metallic Li versus graphite in these electrolytes. The graphite anodes went through formation cycling at low rates (C/25) at room temperature followed by HPPC testing. The cell was then placed in the environmental chamber at  $-30^{\circ}\text{C}$ , subjected to (modified) HPPC testing at  $-30^{\circ}\text{C}$ , then returned to room temperature, and HPPC tested again before the electrodes were removed from the cells and examined by FTIR.

In both electrolytes, the ASI increases by more than one order of magnitude at  $-30^{\circ}\text{C}$  for both charge and discharge processes. The anode potential was considerably more negative during the regenerative charging pulse in the GEN2 *vs.* the EC/PC electrolyte. From FTIR analysis, we were able to arrive at a number of conclusions:

- We definitively identified lithium ethylene dicarbonate as the passive film on metallic Li in EC:EMC/LiPF<sub>6</sub> electrolyte
- The SEI layer on graphite is much more complex than on metallic Li. Lithium ethylene dicarbonate is **not** a primary SEI component. The reaction path leading to the final components is yet to be understood.
- A SEI layer characteristic of metallic Li was observed after HPPC at  $-30^{\circ}\text{C}$  in GEN2 electrolyte, but it was readily washed off by rinsing with DMC. The remaining SEI was identical to that formed at RT. There was clear evidence that Li was deposited on top of the graphite SEI formed at RT, a result that was probably due to a large potential drop in the electrolyte at  $-30^{\circ}\text{C}$ .
- No spectroscopic signature of Li deposition after HPPC at  $-30^{\circ}\text{C}$  in EC:PC:DMC was seen. The SEI composition appears to be identical to that formed in GEN2, possibly thicker. A higher electrode potential during the charge pulse (+0.1 *vs.*  $-0.5\text{ V vs. Li/Li}^{+}$ ) was consistent with spectroscopy. A higher electrolyte conductivity appears to provide an adequate explanation for the absence of Li deposition during charge in EC/PC.
- There is a need to establish general applicability of these conclusions, *i.e.*, using other anode materials and electrolytes.



## TASK STATUS REPORT

**PI, INSTITUTION:** G. Ceder, Massachusetts Institute of Technology  
C. Grey, SUNY at Stony Brook

**TASK TITLE - PROJECT:** Diagnostics - First-Principles Calculations and NMR Spectroscopy of Cathode Materials

**SYSTEMS:** Doped lithium nickel manganese oxides; lithium iron phosphates

**BARRIERS:** Low rate capabilities, high cost, poor stability.

**OBJECTIVES:** Determine the effect of structure on stability of cathodes. Explore rate limitations and relation to structure.

**APPROACH:** Use solid-state NMR to characterize local and diffraction/TEM for long-range structure, as a function of sample preparation method, state of charge, and number of charge cycles. Use first principles calculations (density functional theory) to identify redox-active metals, relative stability of different structures, and the effect of structure on cell voltages; and to identify promising cathode materials for BATT applications. Anticipate possible instabilities in materials at high states of charge by using calculations. Use calculations and NMR to identify low-activation energy pathways for cation migration and to investigate electronic conductivity.

**STATUS OCT. 1, 2004:** The analysis of the local and long-range structures of  $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$  (calculations, diffraction, and NMR) will have been completed. NMR studies of local structure of  $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$  following extended cycling studies will have been completed.

**EXPECTED STATUS SEPT. 30, 2005:** Correlations between  $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$  local and long-range structure and stability will have been completed. Joint NMR/calculations of conduction mechanisms (ionic and electronic) of BATT cathode materials will be underway. Applications of NMR and calculation methodology to other relevant systems under investigation by members of the BATT program will be ongoing.

**RELEVANT USABC GOALS:** Specific power 300 W/kg, 10 year life, < 20% capacity fade

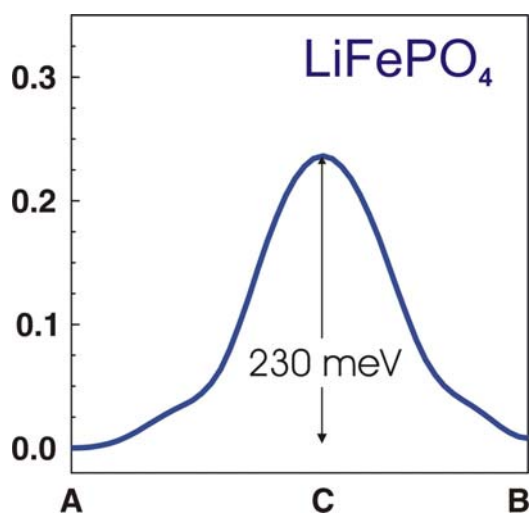
### MILESTONES:

- 1) Complete analysis of x-ray and neutron diffraction of  $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$ . Perform initial tests on conductivity model. (Nov. 1, 2004)
- 2) Complete analysis (NMR, TEM, diffraction) of  $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$  as a function of synthesis method. Examine effect of structure on  $\text{Li}^+$  mobility in  $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$  (calculations/NMR); extension of approach to other BATT systems will be underway. Complete studies of acid-leached  $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$  (Thackeray) and  $\text{Ni}^{3+}$ -doped material (Goodenough). Outline and perform initial test of stability prediction methodology. (May 1, 2005).

## PROGRESS TOWARD MILESTONES

We have continued our combined modeling and experimental work on the  $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$  systems, with particular focus on the structure and rate capability of the  $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$  end member as a potential Co-free replacement for the  $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$  system. First principles modeling had suggested a structure for this material<sup>(1)</sup>. We have now been able to confirm that structure with Transmission Electron Microscopy on well-annealed samples. Neutron-diffraction studies suggest that the samples quenched from high temperature are more disordered, but that some long-range ordering still persists.<sup>(2)</sup> While the relation between transition metal ordering and performance is not yet clear, our initial results indicate that the structure of this material changes significantly upon cycling and that these changes may affect the rate performance. Currently, we are combining NMR, XRD, TEM and first principles modeling to develop a structural model for the changes in this material upon cycling.

Following cycling between 2.5V and 4.6 V, the local structure as probed by Li NMR changes slowly, the concentration of Li in the transition metal layers dropping gradually, so that by 20 cycles no Li in the TM layers remains. The long-range structure (as probed by XRD) changes more rapidly and by 2-3 cycles, evidence for longer-range ordering in the TM layers has disappeared. Similar results are seen for the  $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$  and  $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{5/9}\text{Li}_{1/9})\text{O}_2$ ; however, it is easier to follow the disappearance of long-range order in the Ni 1/3 material. In contrast, when the material is charged to 5.3V essentially all of the Li is removed from the material – both from the Li layers and from the transition metal layers. XRD and neutron studies are in progress to follow the changes in Ni/Mn structure during these processes.



**Figure 1.** Energy path for a polaron transition between two equivalent Fe sites in  $\text{LiFePO}_4$ . The barrier is only about 230 meV, but is significantly increased when the Li vacancy is close to the  $\text{Fe}^{3+}$  hole.

Our theoretical efforts to predict electronic and ionic conductivity in electrode materials (and hence rate capability) are coming to fruition. Figure 1 shows the calculated activation barrier for a free polaron in  $\text{LiFePO}_4$ . While this barrier is reasonably low, we also found that there is a significant association energy between the hole carrier in  $\text{LiFePO}_4$  and the Li vacancy that creates it. This binding energy is of the order of 130 meV. The binding energy and polaron migration barrier would lead to an activation barrier of >400 meV, which is in reasonable agreement with what has been measured experimentally by several groups. We are currently extending the modeling effort to other materials and are constructing a more general predictive capability of ionic and electronic transport in electrode materials. In addition we have started to test a methodology for predicting the oxygen release of electrodes at high states of charge as this will become a part of our BATT project in the next project year.

### Publications:

1. A. Van der Ven, G. Ceder, *Electrochemistry Communications* **6**, (2004) 1045-1050.
2. J. Bréger, N. Dupré, P. J. Chupas, P. L. Lee, Th. Proffen, J. B. Parise, C. P. Grey, *J. Am. Chem. Soc.*, in press (2005).

## TASK STATUS REPORT

**PI, INSTITUTION:** T.M. Devine, Lawrence Berkeley National Laboratory

**TASK TITLE – PROJECT:** Diagnostics – Corrosion of Current Collectors

**SYSTEMS:** Low-cost Li-ion

**BARRIERS:** Uncertain and possibly inadequate corrosion resistance of Al current collectors

**OBJECTIVES:** Determine the influence of corrosion and passivation of Al current collectors on the capacity loss of Li-ion batteries. Determine the effect of water contamination of battery electrolytes on the corrosion and passivation of Al current collectors. Compare/contrast the corrosion and passivation of Al in battery electrolytes with salts of  $\text{LiPF}_6$  and  $\text{LiBOB}$ .

**APPROACH:** This project consists of three tasks, which are worked on in parallel. In Task 1, the influence of corrosion and passivation of Al current collectors on battery capacity loss is quantitatively evaluated. Three conditions of the Al current collectors are investigated: 1) Al covered with an air-formed film of  $\text{Al}_2\text{O}_3$ , which is the current collector's surface condition in an unused battery; 2) Al covered with a duplex surface film consisting of an inner layer of air-formed  $\text{Al}_2\text{O}_3$  and an outer layer of  $\text{AlF}_3$ , which is the surface condition that might develop after a number of charge/discharge cycles in  $\text{LiPF}_6$  electrolytes; 3) Al covered with a 1- $\mu\text{m}$  thick anodized film of  $\text{Al}_2\text{O}_3$ , which is a surface condition that earlier work has shown to exhibit excellent corrosion resistance. In all three cases the current collectors are coated with cathodes of  $\text{LiFePO}_4$ . In Task 2, concentrations of water ranging from 2 to 100 ppm are deliberately added to battery electrolytes with salts of  $\text{LiPF}_6$  and  $\text{LiBOB}$  to investigate the influence of water contamination on the corrosion and passivation of Al current collectors. In Task 3, electrochemical tests and *in situ* Raman spectroscopy are employed to probe the mechanism of corrosion of Al current collectors. Task 3 provides the mechanistic understanding of the corrosion phenomena that contribute to battery capacity loss as determined in Task 1.

**STATUS OCT. 1, 2004:** Aluminum electrodes with anodized films formed in sulfuric acid (to produce 1- $\mu\text{m}$  thick layer of  $\text{Al}_2\text{O}_3$ ) and in battery electrolytes (to produce a duplex film with outer layer of  $\text{LiPF}_6$ ) will be prepared and coated with cathodes of  $\text{LiFePO}_4$  (Task 1). An electrochemical technique, which was proposed by Tobias and colleagues, will be evaluated as a tool for measuring small quantities of water (1-10 ppm) in battery electrolytes containing EC, DMC, and PC as solvent (Task 2). The electrochemical cell for *in situ* Raman spectroscopy of Al in battery electrolytes will be designed and constructed along with optics to direct laser light onto the Al sample and to collect Raman-scattered light from the Al sample (Task 3). Inspection of current collectors from life-tested coin cells will continue with an emphasis on cells that utilized new electrolytes (*e.g.*, salt of  $\text{LiBOB}$ ) (Task 1).

**EXPECTED STATUS SEPT. 30, 2004:** The contribution of corrosion of current collectors to battery overall capacity loss will be quantitatively expressed. The mechanism of passivation of Al and the identity of the passive film of Al will be determined in battery electrolytes that contain  $\text{LiBOB}$ . The possible role of particular cathodes in causing corrosion of Al current collectors in electrolytes with  $\text{LiPF}_6$  and  $\text{LiBOB}$  will be identified. The likelihood of corrosion of Al current collectors in  $\text{LiBOB}$  electrolytes will be compared to the susceptibility of Al current collectors to corrosion in  $\text{LiPF}_6$  electrolytes.

**RELEVANT USABC GOALS:** 10 year life; < 20% capacity fade.

**MILESTONES:** 1) Determine influence of water contamination on the resistance of cathode-coated Al to corrosion in battery electrolytes with salts of  $\text{LiPF}_6$  and  $\text{LiBOB}$ . (8/05). 2) Determine relevance of Al's susceptibility to corrosion on battery capacity loss. (8/05)

## PROGRESS TOWARD MILESTONES

During the past quarter work was focused on determining the details of the mechanism of corrosion of Al current collectors in Li-ion batteries. Our earlier results had indicated that corrosion of Al current collectors occurred by a process called underdeposit corrosion, which is a type of crevice corrosion. Underdeposit corrosion of Al current collectors is a consequence of the microscopic porosity of the cathodes that cover the Al. While microporous cathodes act as crevice formers of Al, a polyethylene disk with radially oriented grooves was found to not cause crevice corrosion of Al in Li-ion battery electrolytes. The inability of polyethylene to act as a crevice former suggested that the battery's cathodes play an active role in the crevice corrosion of Al. For example, the cathodes cause local changes in the electrolyte's composition, which becomes corrosive to Al.

An extensive review of the published literature indicated that the topic of "passive film" formation on cathodes and the stability of the electrolyte against oxidation on the cathode surface are topics of ongoing research. Nevertheless, at the operating voltages during battery charging there is no compelling evidence in the literature of (1) catalytic oxidation of battery electrolytes on the cathode's surface, nor (2) the formation of corrosive oxidation products. Furthermore, our research had found corrosion of Al current collectors independent of which of three types of cathodes were employed. It seems unlikely that all three cathodes would be equally effective at oxidizing the electrolyte and generating corrosive products.

A possible basis for the direct role of the cathode in causing crevice corrosion of Al current collectors is related to the cathode acting as a source of water. Water leached from the cathode would increase the water's concentration in the micropores of the cathode. Hydrofluoric acid (HF), which is highly corrosive to Al, would be formed in the pores by hydrolysis of the electrolyte's salt, LiPF<sub>6</sub>. For example, the binder, PDvF, which is common to all the cathodes we have studied, contains water as an impurity (890 ppm of water).

To determine if water concentrations, which lead to HF, might cause significant corrosion of Al, a large number of electrochemical tests (anodic and cathodic polarization, cyclic voltammetry, rotating disk electrodes, electrochemical impedance spectroscopy, and electrochemical quartz crystal microbalance measurements) have been conducted on four different grades/alloys of Al: 99.999% Al, 1100 Al (99%), Al foil (98.5%), and 2024 Al. In addition, to help determine the identities of the oxidation and reduction processes occurring on the surfaces of the Al samples, a nearly equal number of electrochemical tests were conducted on electrodes of Pt.

To confirm the corrosive effects of dilute quantities of HF, preliminary experiments were conducted in aqueous solutions. Very small concentrations of HF (*e.g.*,  $2 \times 10^{-3}$  M) were able to completely destroy the Al's passive film, which consists mostly of alumina (Al<sub>2</sub>O<sub>3</sub>). The air-formed film of Al<sub>2</sub>O<sub>3</sub> is largely responsible for the corrosion resistance of Al current collectors in battery electrolytes.

The battery of previously listed electrochemical tests have been conducted on the four grades/alloys of Al and Pt electrodes in five different organic electrolytes, all of which contain the salt LiPF<sub>6</sub>: Gen3, 0.4M LiPF<sub>6</sub> in EC+PC+DMC (with no deliberate addition of water and with deliberate additions of 45 ppm, 50 ppm, 73 ppm, 81 ppm, and 171 ppm water), 0.35M LiPF<sub>6</sub> in PC (2 ppm, 874 ppm, 4000 ppm water), 0.38M LiPF<sub>6</sub> in DMC, and 0.38M LiPF<sub>6</sub> in EC+DMC (2469 ppm).

We are still in the process of examining the results of the electrochemical tests. Preliminary analysis indicates that high concentrations of water do not lead to excessive corrosion of the Al. If the tentative conclusion that high concentrations of water are not corrosive to Al in battery electrolytes holds up, it will be necessary to re-exam the structure of the composite cathode for additional clues regarding the cathode's role in the corrosion of current collectors.

## **BATT TASK 6 MODELING**

### **TASK STATUS REPORT**

**PI, INSTITUTION:** J. Newman, Lawrence Berkeley National Laboratory

**TASK TITLE – PROJECT:** Modeling - Improved Electrochemical Models

**SYSTEMS:** High-voltage, high-energy: Gr/LiPF<sub>6</sub>+EC:DEC/LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>  
Low-voltage, high-stability: Gr/LiPF<sub>6</sub>+EC:DEC/LiFePO<sub>4</sub>  
High-voltage, high-power: Gr/LiBOB+γBL:EA/LiMn<sub>2</sub>O<sub>4</sub>

**BARRIERS:** Poor transport properties, capacity and power fade

**OBJECTIVES:** Develop experimental methods for measuring transport and thermodynamic properties. Model electrochemical systems to optimize performance, identify limiting factors, and mitigate failure mechanisms.

**APPROACH:** Use simulations to improve understanding of the SEI layer and particle volume expansion. Develop improved experimental methods for measuring transference numbers in liquid electrolytes.

**STATUS OCT. 1, 2004:** Modeling of dendrite growth is complete. A stability analysis that determines practical conditions under which dendrite growth can be inhibited or eliminated by mechanical means is complete. Comparison of SEI simulations with experimental results and refinement of the model is ongoing. Full characterization of transport in LiPF<sub>6</sub> electrolytes is ongoing.

**EXPECTED STATUS SEPT. 30, 2005:** Work will continue on a model for calculating stress distributions in electrode materials during intercalation. Full characterization of transport in LiPF<sub>6</sub> electrolytes will be ongoing. New projects may begin either on active material connected to a current collector and/or on including the Ni-MH system on the dualfoil model platform with side reactions.

**RELEVANT USABC GOALS:** 30 ohm-cm<sup>2</sup> area-specific impedance, cold cranking capability to -30°C, 300,000 shallow discharge cycles, abuse tolerance to cell overcharge and short circuit

**MILESTONES:** Model for calculating stress distributions in electrode materials during intercalation will be completed. (Dec. 2004)

## **PROGRESS TOWARD MILESTONES**

### **Particle Expansion and Fracture**

We have formulated a mathematical model of particle volume expansion, which is used to calculate stress profiles in active electrode material due to Li insertion. Results indicate that graphite particles will possibly fracture at high charge rates typical of hybrid-electric vehicle applications, but are unlikely to fracture at low to moderate rates. Refinements to the model include the influence of nonidealities in the solid solution upon the electrode kinetics and thermodynamic factor, both of which influence the stress that is generated in the particle. Lithium insertion and extraction under potentiostatic and galvanostatic conditions have been successfully simulated with the model. Experiments have begun in order to investigate the degradation of graphite at high charge rates.

### **Transport Property Measurement**

The development of an anion-reversible electrode has continued for  $\text{LiPF}_6$  electrolytes of interest. A new chemistry is being considered. This reference electrode will be used in EMF measurements in order to determine activity coefficients independently. These measurements will enable a more accurate determination of the transference number as a function of electrolyte concentration in these systems. New methods are being developed in order to avoid the effects of side reactions in diffusion-coefficient measurements. Transference-number measurements, when combined with remaining transport-property data, will allow for a full comparison of transport in different electrolytic solutions.

## TASK STATUS REPORT

**PI, INSTITUTION:** V. Srinivasan and J. Newman, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Modeling - Modeling of BATT Program Baseline Chemistries

**SYSTEMS:**  $\text{LiFePO}_4$ ,  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  and  $\text{LiMn}_2\text{O}_4$

**BARRIERS:** Low power capability; capacity/power fade; poor low-temperature operation

**OBJECTIVES:** 1. Evaluate performance of the three baselines under HEV operation; identify the limiting mechanism in each chemistry. 2. Understand limitations of baselines when operating below room temperature. 3. Investigate degradation mechanisms and begin development of a cycle-life model.

**APPROACH:** Develop mathematical models for the BATT baselines. Perform experiments to complement models and extract unknown parameters. Optimize models to satisfy the EV and HEV goals, and use them to compare the baselines to each other. Perform experiments at lower temperatures and use model to understand the limiting processes. Incorporate life-limiting mechanisms into the models.

**STATUS OCT. 1, 2004:** Models for all three baselines have been completed and the performance limitations identified. A theoretical comparison of the three over a wide discharge range was ongoing.

**EXPECTED STATUS SEPT. 30, 2005:** Modeling of the baselines for HEV applications and optimization studies will be complete. Experimental measurement of kinetic and transport properties at lower temperatures ( $< \text{RT}$ ) will be ongoing. Modeling of low-temperature operation will be ongoing.

**RELEVANT USABC GOALS:**  $\text{ASI} = 30 \text{ } \Omega\text{-cm}^2$ , Cold cranking capability to  $-30^\circ\text{C}$ ; 300,000 shallow discharge cycles

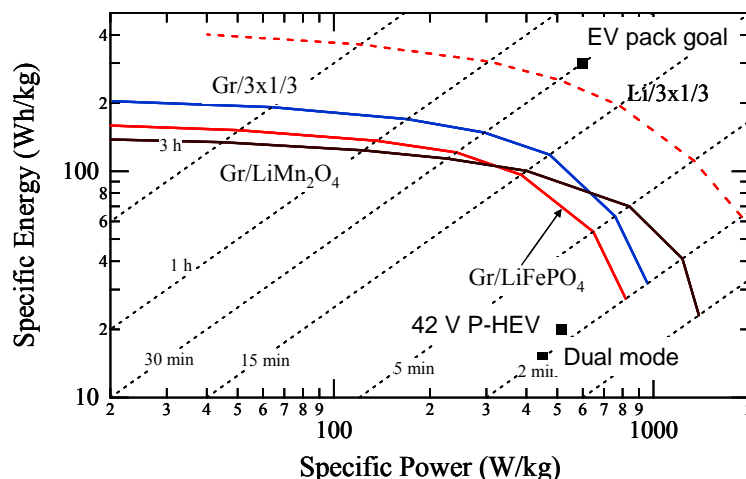
**MILESTONES:**

1. Compare the three baselines under full discharge-time range. (Dec. 2004)
2. Identify the best baseline and the optimal design for HEV applications. (Aug. 2005)

## PROGRESS TOWARDS MILESTONES

### Comparison of the Baselines:

The main focus of this project is to model the three BATT baselines and develop the tools to compare them to each other and to the DOE goals. This task is now complete and is summarized in the Ragone plot below. The graph shows the simulations for the three baselines (namely  $\text{LiFePO}_4$ ,  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  and  $\text{LiMn}_2\text{O}_4$ ) vs. a natural graphite anode with 10% excess anode capacity and for the  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  cathode charged to 4.3 V with a Li metal anode with two times excess anode capacity. The electrolyte in all cases corresponds to 1M  $\text{LiPF}_6$  in 1:1 EC:DEC. The Li-metal simulations were performed on a cell that has the same liquid electrolyte, but with the Li covered with a single-ion conducting glass described in Patent application No. US 2004/0191617 A1 by the Polyplus Battery Company. The resistance of the glass layer (taken from this patent) is included in the model. The lines were generated using the model by optimizing the thickness and porosity of the electrodes for a wide range of discharge-times (corresponding to the sloped lines). Therefore, the design of the cell for a 3 h application is significantly different from that for a 2 min application.



The graph shows the advantage of using the spinel for HEV applications and also allows us to quantify the improvements needed in the other two cathodes for them to be competitive with the spinel. It is clear that the layered material may prove to be an ideal HEV material, if the other attributes that make a good battery (cost, life, and abuse tolerance) are acceptable. However, it is clear from the graph that all graphite-based systems have little hope of achieving the EV needs. Li-metal based systems offer hope in this regard, assuming that the metal can be protected from side reactions and from the formation of dendrites.

### HEV Modeling:

While the above graph shows simulations based on optimizing the performance for a fixed time-of-discharge from 0% to 100% DOD, HEV designs have pulses and a more limited cycling range. In order to simulate this behavior we have used the model to follow the HEV protocol described by the FreedomCAR testing manual. Taking the spinel system as an example, we have simulated the ASI of the cell vs. SOC, and the cumulative energy vs. SOC, from which we have calculated plots of available energy vs. peak power. This plot can be thought of as an equivalent plot to a Ragone plot and will be used as a basis to understand the impact of changing the voltage cut-offs, differences in the rate capability between charge and discharge, effects of thickness and porosity of electrodes, and the impact of the SOC range of cycling.



## TASK STATUS REPORT

**PI, INSTITUTION:** A.M. Sastry, University of Michigan

**TASK TITLE - PROJECT:** Modeling – Scale-Bridging Simulations of Active Materials in Li-ion Batteries, and Validation in BATT Electrodes

**SYSTEMS:** Li/polymer and low-cost Li-ion

**BARRIER:** Short lithium battery lifetimes

**OBJECTIVES:** Determine superior composition and processing conditions of electrodes for conductivity enhancement, especially for the  $\text{LiFePO}_4$  cathode. Develop scale-bridging simulations that will allow identification of the best particle morphologies for both energy- and power-dense systems. Develop superior anodes and cathodes by altering the content and morphologies of conductive materials.

**APPROACH:** Using new simulations developed to model conductivity of the particle networks within both anodes and cathodes, we will expand our investigations with three major new thrusts: 1) development of scale-bridging models to determine likely electrochemical performance of cathode materials, taking direct account of the effects of particle shape and connectivity; 2) determination of the effect of mechanical compression on real batteries, accounting for both multiple layers and cell compression, and 3) extensive experimental and numerical simulation of conduction in new materials synthesized by other BATT workers (Striebel, Zaghib, Wheeler), and provision of guidance concerning the best morphologies to use.

**STATUS OCT. 1, 2004:** Experiments (LBNL and UM) and simulations on conduction and electrochemical performance in baseline anodes and cathodes, with correlations developed relating material composition, SEI layer formation, and cell capacity losses will be completed. Modeling of other BATT Program baseline chemistries will be ongoing.

**EXPECTED STATUS SEPT. 30, 2005:** Correlation of cathode performance with particle morphology, including fiber additives will be made. Completion of conductivity and mechanical experiments to quantify losses under realistic loads will be made.

**RELEVANT USABC GOALS:** Specific power 300 W/kg, 10 year life, <20% capacity fade

### MILESTONES:

- 1) Provision of codes for numerical estimates of conductivity with a wide range of fibrous additives to other BATT workers. (Dec. 2004)
- 2) Development of full, finite element simulations of deformation of carbon additives under realistic loads will be completed. (Jan. 2005)
- 3) Implementation of algorithms to allow correlation of particle shape and size with electrochemical performance in Li-ion cells. (June 2005)
- 4) Experimental testing and numerical prediction of the effect of fibrous carbons on conductivity in  $\text{LiFePO}_4$  cathodes (with materials from Battaglia, Zaghib, Wheeler). (June 2005)

## PROGRESS TOWARD MILESTONES

### • Accomplishment toward milestone over last quarter

Last quarter, we developed a strategy for implementing a combined molecular dynamics/continuum finite element model for the baseline electrochemistry. Our approach uses computational fluid dynamics, mass transport, and reaction rate to determine response of the system. This approach has extended our previous stochastic approach and has the following goals:

1. Map the effects of morphology of electrode on transport mechanisms within a cell, to provide guidance in selecting particle sizes and manufacturing processes;
2. Map the effects of conductive additives on the transport mechanism within a cell, to provide guidance for optimizing amounts of additives required for improvement of high-rate performance without sacrificing the energy density; and
3. Simulate distribution of potential and current density within each electrode, to provide estimation of reaction rate.

Our technique begins with generation of a realistic morphology of electrode via use of a collision algorithm, incorporating controllable stochastic distribution of particle sizes, and locations. We have also identified key elements of our mathematical model that will incorporate fluid dynamics, and thermodynamics information allowing simulation of batteries.

We have chosen the commercial package FEMLAB © as a tool for simulation of batteries. FEMLAB is commonly used, and has the capability to perform multiphysics analyses. With the incorporation of our algorithm into FEMLAB, the designer will have a tool to visualize and test new electrode configurations. We are at the stage of testing this technique with a single intercalation porous electrode, or two intercalation porous electrodes of Li-ion batteries.

### • Further plans to meet or exceed milestone

We will continue developing the mathematical model for analysis of baseline materials, and plan to integrate with other DOE workers as validation of models, and in order to continue to provide guidance on selection/design of materials.

### • Reason for changes from original milestone: N/A

## PROPOSALS UNDER REVIEW

<b>ORGANIZATION</b> <i>(Principal Investigator)</i>	<b>TITLE</b>	<b>STATUS</b>
Carnegie Mellon University <i>(P. Kumta)</i>	High capacity, reversible encapsulated porous nanocomposite anodes for lithium-ion batteries	Unsolicited Proposal-Under Review
Bar-Ilan University <i>(D. Aurbach)</i>	Development and study of the high temperature performance of Li-ion batteries for EV application	Unsolicited Proposal-Rejected
Michigan Technological University <i>(B. Cornilsen et al.)</i>	Characterization of the cathode structures and nonstoichiometry to improve properties of the Mn-containing, Li-ion, Baseline Cathodes	Unsolicited Proposal-Rejected
Massachusetts Institute of Technology <i>(Y. Shao-Horn)</i>	TEM and AFM studies of nanoparticle coating on lithium battery materials: its effect on electrode stability, battery cycle life and battery safety	Unsolicited Proposal-Under Review
University of South Carolina <i>(J. Weidner)</i>	Advanced analysis of electrochemical impedance spectra to measure transport properties in Li-ion batteries	Unsolicited Proposal-Rejected
Graz University of Technology <i>(M. Winter)</i>	Investigations on safety and performance of intermetallic anodes of the BATT program in organic electrolytes by <i>on-line</i> mass spectrometry	Unsolicited Proposal-Under Review

## **BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT) CALENDAR OF RECENT AND UPCOMING EVENTS**

### May 2005

- 15 - 20 207th Electrochemical Society Meeting – Quebec City, Canada (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; [ecs@electrochem.org](mailto:ecs@electrochem.org); <http://www.electrochem.org/meetings/meetings.htm>)
- 22 - 27 Lithium Battery Discussion Meeting, LiBD2004 – Arcachon France (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; [ecs@electrochem.org](mailto:ecs@electrochem.org); email: [Josh.Thomas@mkem.uu.se](mailto:Josh.Thomas@mkem.uu.se); <http://www.icmcb.u-bordeaux.fr/libd>)

### June 2005

- 12 - 17 2nd International Conference on Polymer Batteries and Fuel Cells – Las Vegas, NV (Broddarp of Nevada, Inc. and The Electrochemical Society, 792-897-3027, [dbrodd@broddarp.com](mailto:dbrodd@broddarp.com)) Riviera Hotel and Casino
- 13 - 17 5th International Advanced Automotive Battery Conference (AABC-05) on VRLA for Traction Applications, and International Symposium on Large Lithium Battery Technology and Application (LLIBTA) – Honolulu HI (Menahem Anderman, Conf. Chair; <http://www.advancedautobat.com>) Sheraton Waikiki Beach Resort

### September 2005

- 25 - 30 56<sup>th</sup> Annual Meeting of the International Society of Electrochemistry – Busan, Korea (Contact: H Kim; [hasuckim@plaza.snu.ac.kr](mailto:hasuckim@plaza.snu.ac.kr))

### October 2005

- 16 - 21 208th Electrochemical Society Meeting – Los Angeles, CA (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; [ecs@electrochem.org](mailto:ecs@electrochem.org); <http://www.electrochem.org/meetings/meetings.htm>)

### May 2006

- 7 - 12 209th Electrochemical Society Meeting – Denver, CO (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; [ecs@electrochem.org](mailto:ecs@electrochem.org); <http://www.electrochem.org/meetings/meetings.htm>)
- 23 - 29 Lithium Battery Discussion Meeting, LiBD2004 – Arcachon France (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; [ecs@electrochem.org](mailto:ecs@electrochem.org); email: [Josh.Thomas@mkem.uu.se](mailto:Josh.Thomas@mkem.uu.se); <http://www.icmcb.u-bordeaux.fr/libd>)

### October 2006

- 29 - Nov. 3 210th Electrochemical Society Meeting – Cancun, Mexico (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; [ecs@electrochem.org](mailto:ecs@electrochem.org); <http://www.electrochem.org/meetings/meetings.htm>)